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ADVANCED LECTURE NOTES ON HEAT

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ADVANCED LECTURE NOTES ON HEAT

BY

J. R. ECCLES, M.A.

HEADMASTER OF GRESHAM'S SCHOOL, HOLT

OF TORONTO LI
UNIVERSITY

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PREFACE

THIS book is a sequel to *Lecture Notes on Heat* published privately in 1913. Though the method adopted is, in the main, similar, the present volume approximates more to a text-book, owing to the difficulty of presenting the more advanced part of the subject in the concise form possible with the elementary portion.

J. R. E.

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THERMOMETRY

Measurement of Temperature

The temperature of a body is a measure of its thermal potential, i.e. of its condition with regard to its power of giving heat to or receiving heat from other bodies. Two bodies are said to be at the same temperature when their thermal potentials are the same, i.e. when their conditions are such that they have the same tendency to give heat to or receive heat from another body or other bodies.

In order to ascertain when two bodies are at the same temperature, it is customary to allow heat to flow from each body in turn into a "receiver" of *small* heat capacity—small, so that the bodies shall not lose an appreciable amount of heat and their temperature shall not alter appreciably—in which some physical change is brought about, to an extent depending upon the quantity of inflowing heat, until the "receiver" is at the same temperature as the body. Such a "receiver" is called a "thermometer." Thus two bodies are said to be at the same temperature when the heat abstracted, say, by the bulb of a mercury-in-glass thermometer in contact with the first body, causes the same expansion of the mercury and glass as the heat abstracted by contact with the second body, or when the heat withdrawn by a platinum wire causes the same increase in electrical resistance in the case of a platinum resistance thermometer.

In order to compare the difference in temperature between two bodies, it is necessary to compare the amounts of the change brought about in some standard physical change. To do this it is necessary both to define certain fixed temperatures and also to divide up the distance between them.

To define certain fixed temperatures use is made of the fact that the physical state of a body depends upon the temperature. It is found that, during the change from one state to another, the temperature remains constant. The temperatures at which a given substance, under given conditions, changes its state are used as "fixed points" on a scale of temperature. The "lower fixed point" of most scales is the temperature of melting ice under standard atmospheric pressure. The "upper fixed point" is the temperature of steam issuing from water boiling under standard atmospheric pressure. The former is called the "Freezing Point" and the latter the "Boiling Point."

In order to subdivide the interval between these two fixed points, use is made of the change in volume of some fluid, usually mercury or hydrogen, which occurs with change of temperature. Now there is no *a priori* reason for supposing that the rate of change of volume of a substance, such as mercury, with temperature is the same at all temperatures. (It is well known that it is not so in the case of water.) Since, however, we have for the moment no special means of measuring temperature as distinct from the effects of temperature upon the physical properties of bodies (see "Lord Kelvin's Absolute

Scale of Temperature"), we shall assume that the rate of change of some fixed property of some standard substance *is* constant and use this change to subdivide the temperature between the two fixed points. For this purpose we take the change in volume of mercury-in-glass, i.e. mercury contained in a glass vessel, as the means of defining the temperature between the two fixed points.

Let l be the apparent increase in length of the column of mercury in a capillary tube, of uniform bore, attached to a glass bulb containing mercury, when the bulb is put first in melting ice and then in steam. Then the interval in temperature which causes the mercury thread to rise through a distance $l/100$ is called, in the case of the "Centigrade scale," a "Centigrade degree," and is indicated by the symbol 1 C.° Or, to put it in another way, let v be the apparent increase in volume of a given mass of mercury, enclosed in a glass envelope, consisting of a bulb and capillary tube, when the bulb is put first in melting ice and then in steam. Then the interval in temperature which causes this mass of mercury to expand by an amount $v/100$ is called a "Centigrade degree."

On the Centigrade scale the temperature of melting ice is 0° C. and that of boiling water 100° C., the interval being divided into 100 equal divisions or degrees. Then a body which causes the mercury thread to reach the 15th degree is said to differ by 50 degrees on the mercury-Centigrade scale from a body which causes the thread to reach the 65th degree. Hence we may *define* temperature on the mercury-Centigrade scale as the point on the scale of 100 equal divisions to which the thread of a mercury thermometer, calibrated in melting ice and steam at standard atmospheric pressure, will reach when it is placed in the region where the temperature is to be measured.

For temperatures below that of melting ice the scale is continued downwards, the sign *minus* being prefixed. Thus a temperature such that the volume of the given mass of mercury is, say, $5v/100$ less than that at 0° C. is indicated by -5° C. In a similar way the scale is continued above 100° C.

In the case of the Fahrenheit scale an exactly similar process is carried out, except that a Fahrenheit degree, or 1 F.°, corresponds to a rise in length of $l/180$ or an increase in volume of $v/180$, i.e. the distance between the Freezing Point and Boiling Point is divided into 180 equal divisions. The temperature of melting ice on this scale is 32° F. and that of boiling water 212° F.

It is clear, too, that the expansion of mercury with increase in temperature and the increase in the electrical resistance of a platinum wire are not the only possible physical changes that may be used to compare temperatures or thermal potentials. These changes are usually used in thermometry because they are found to be "linear" functions of the temperature and hence are to be preferred to changes such as the variation in the pressure of aqueous vapour with temperature, which is not "linear."

EXPANSION OF SOLIDS

To determine the coefficient of Linear Expansion of a Solid

I. Shaw's Method

(See Elementary Notes)

Disadvantages of Shaw's method:—

(1) The temperature of the tube is not the same inside and out.

(2) The temperature taken by the thermometers is not the temperature of the tube, but of the steam or water, as the case may be.

(3) It is impossible to use the method satisfactorily for a variety of temperatures.

II. Weedon's Method

The apparatus consists of the following parts:—

1. A long zinc trough containing water, in which is placed the rod, 1 metre long, the expansion of which is to be measured.

2. A gas burner supported beneath the trough and running the whole length of it, by means of which the water in the trough can be heated.

3. Two delicate micrometers, fixed on rigid supports at either end of the trough.

4. Two short glass rods passing through stuffing-boxes at the ends of the trough, abutting on one side against the ends of the metal rod and on the other against the micrometers.

5. A metal screen, at each end, faced inside with asbestos, to prevent heat from radiating to the micrometers.

6. Two supports for the trough, placed in a cold water trough, provided with inlet and exit pipes, and running the whole length of the base, to prevent any expansion of the base and supports.

The experiment is conducted as follows:—

The micrometers are screwed back sufficiently far to permit the maximum expansion of the bar. The burner is lighted and the water in the trough raised to boiling point. When the maximum temperature is reached, one micrometer is screwed in until

the screw comes in contact with the glass end-piece. The other micrometer is then screwed up very carefully until it is *felt* to just grip the glass end-piece. The readings of both micrometers must be taken. The gas burner is then lowered and observations taken for other temperatures. Readings may be taken for differences of 10 C.° from 100° C. to 20° C.

Advantages of Weedon's method:—

(1) The bar is *presumably* at the temperature of the water.

(2) The temperature of the bar can be varied.

(3) Special precautions are taken to guard against any transference of heat by conduction and radiation.

Disadvantages of Weedon's method:—

(1) It is very difficult to keep the water at a uniform temperature.

(2) The arrangement by which the glass end-pieces pass through stuffing-boxes is not a very satisfactory one.

(3) The method of adjustment of the micrometers by touch is not nearly as sensitive as electrical contact.

III. Calvert's Method

The apparatus consists of the following parts:—

1. A metal bar, supported along the axis of a jacket tube at two points some distance from the ends, so that errors due to sagging may be reduced to a minimum.

2. Two short pieces of invar are arranged at the ends of the bar. One passes out through one cork of the jacket and presses against a fixed stop on the base of the apparatus. The other passes loosely through the other cork of the jacket and is carried in a short length of brass tubing, which forms a bearing and is clamped to a support fixed to the base of the apparatus.

3. A spring, attached to the brass tube and the piece of invar, presses the latter up against the end of the bar.

4. A micrometer microscope, which is focussed on to a fine scratch on the piece of invar. The movement of the scratch gives the expansion of the bar, since the expansion of the invar is negligible.

Advantages of Calvert's method:—

(1) The bar is completely surrounded by steam in the jacket, so that its temperature is correctly given by the reading of the thermometer in the jacket.

(2) One bar can be readily replaced by another, a single screw releasing the brass tube, which carries the piece of invar, and so allowing the jacket to be removed.

IV. Roy and Ramsden's Method

This method dates back to the year 1785, and is mainly of historical interest.

Three troughs *AB*, *CD*, *EF*, each about 5 ft. long, were placed approximately parallel to one another, as shown in the figure. The middle trough, *CD*, contained the bar, the expansion of which was to be determined, whilst the two outside troughs contained standard bars, maintained throughout the experiment at a constant temperature, by being surrounded with melting ice. These standard bars carried uprights. Those attached to the bar in *AB* were provided with cross-wires, A_1, B_1, whilst those attached to the bar in *EF* carried eye-pieces E_1, F_1. The eye-piece, E_1, was provided with fixed cross-wires, whilst the eye-piece, F_1, was provided with cross-wires which could be moved by a delicate micrometer screw. The central bar had uprights attached to it carrying object-glasses C_1, D_1. Each object-glass, together with the corresponding eye-piece, formed a microscope, by means of which the cross-wires A_1, B_1 could be viewed.

The experiment was conducted as follows:—

All the three troughs were filled with melting ice and the eye-pieces E_1, F_1 adjusted so that the cross-wires, which they carried, were brought into coincidence with the images of the cross-wires A_1, B_1, respectively. The middle trough, *CD*, was then filled with water, which was kept boiling briskly. The contained bar expanded and the object-glasses C_1, D_1 were consequently displaced.

The trough *CD was moved bodily* till the image of the cross-wires, A_1, was again brought into coincidence with the cross-wires in E_1. The image of the cross-wires, B_1, was then found to be displaced relatively to the cross-wires in F_1. This displacement was measured by moving the cross-wires in F_1 by means of the micrometer screw, until coincidence was once more obtained. The distance through which the object-glass, D_1, was displaced was equal to the expansion of the bar. This displacement was less than the distance measured by the micrometer in a fixed ratio, as the diagram shows.

Displacement of object-glass $D_1 = D_1D_2$.

Displacement measured by micrometer $= F_1F_2$.

Then, by similar triangles,

$$\frac{D_1D_2}{F_1F_2} = \frac{B_1D_1}{B_1F_1}.$$

$$\therefore\ D_1D_2 = F_1F_2 \times \frac{B_1D_1}{B_1F_1}.$$

This gives the expansion of the bar.

It has since been pointed out that, if F_1 had been provided with fixed cross-wires and the object-glass, D_1, had been moved by a micrometer screw, till the image of the cross-wires, B_1, was brought into coincidence with the cross-wires in F_1, the distance registered by the micrometer would have been equal to the expansion of the bar.

Effect of change of temperature upon the time of swing of a Pendulum

Examples

1. A clock keeps correct time at 0° C. but loses 37·35 secs. per week at 10° C. Find the coefficient of linear expansion of its pendulum.

We know that

$$t_1 = 2\pi\sqrt{\frac{l_1}{g}},$$

$$t_2 = 2\pi\sqrt{\frac{l_2}{g}}.$$

$$\therefore \frac{t_1}{t_2} = \sqrt{\frac{l_1}{l_2}},$$

$$\frac{l_1}{l_2} = \frac{t_1^2}{t_2^2}.$$

Loss in time per week = 37·35 secs.

No. of swings per week at 0° C. = 7 × 24 × 60 × 60
= 604800.

No. of swings per week at 10° C. = 604800 – 37·35
= 604762·65.

$$\therefore t_1 = \frac{1}{604800} \text{ week},$$

$$t_2 = \frac{1}{604762{\cdot}65} \text{ week}.$$

$$\therefore \frac{t_1}{t_2} = \frac{604762{\cdot}65}{604800}.$$

Now we have seen that

$$\frac{l_1}{l_2} = \frac{t_1^2}{t_2^2}.$$

$$\therefore \frac{l_1}{l_2} = \left(\frac{604762{\cdot}65}{604800}\right)^2.$$

$$\therefore \frac{l_2}{l_1} = \left(\frac{604800}{604762{\cdot}65}\right)^2$$

$$= 1{\cdot}000124.$$

But $$l_2 = l_1(1 + at).$$

$$\therefore \frac{l_2}{l_1} = 1 + at.$$

$$\therefore 1 + at = 1{\cdot}000124.$$

$$\therefore at = {\cdot}000124.$$

$$\therefore a = \frac{{\cdot}000124}{t}$$

$$= \frac{{\cdot}000124}{10}$$

$$= {\cdot}0000124.$$

Coefficient of linear expansion of pendulum

$$= {\cdot}0000124.$$

2. A clock with an iron pendulum is made so as to keep correct time at 5° C. How will its rate alter if the temperature rise to 30° C.?

We know that

$$l_2 = l_1(1 + at)$$

$$= l_1[1 + ({\cdot}000012 \times 25)]$$

$$= l_1(1 + {\cdot}0003)$$

$$= l_1 \times 1{\cdot}0003.$$

We have seen that

$$\frac{t_1}{t_2} = \sqrt{\frac{l_1}{l_2}}.$$

$$\therefore \frac{t_1^2}{t_2^2} = \frac{l_1}{l_2}.$$

$$\therefore \frac{t_2^2}{t_1^2} = \frac{l_2}{l_1}.$$

But $$t_1 = 1 \text{ sec.}$$

$$\therefore t_2^2 = \frac{l_2}{l_1}$$

$$= \frac{l_1 \times 1{\cdot}0003}{l_1}$$

$$= 1{\cdot}0003.$$

$$\therefore t_2 = \sqrt{1{\cdot}0003}$$

$$= 1{\cdot}00015 \text{ sec.}$$

$$\text{No. of swings per week} = \frac{\text{total time}}{\text{time of 1 swing}}$$

$$= \frac{604800}{1{\cdot}00015}$$

$$= 604709{\cdot}29.$$

$$\therefore \text{ Loss in time per week} = 604800 - 604709{\cdot}29$$

$$= 90{\cdot}71 \text{ secs.}$$

∴ Clock loses 90·71 secs. per week.

$$\text{Loss in time per day} = \frac{90{\cdot}71}{7}$$

$$= 12{\cdot}96 \text{ secs.}$$

The clock loses 12·96 secs. per day.

[Note that, if we wished to be very precise, we might take the length at 5° C. and 30° C. to be

$$l_1(1+5a)$$

and

$$l_1(1+30a),$$

since the coefficient at 5° C. will not be quite the same as at 0° C.]

3. A clock, which keeps correct time at 25° C., has a pendulum rod made of brass. How many secs. a day will it gain, if the temperature fall to the freezing point?

Let $l_1 = \text{length at } 0^\circ \text{ C.},$

$l_2 = \text{length at } 25^\circ \text{ C.}$

We know that

$$l_2 = l_1(1+at)$$

$$= l_1[1 + ({\cdot}000019 \times 25)]$$

$$= l_1(1 + {\cdot}000475)$$

$$= l_1 \times 1{\cdot}000475.$$

We have seen that

$$\frac{t_1^2}{t_2^2} = \frac{l_1}{l_2}.$$

But $t_2 = 1 \text{ sec.}$

$$\therefore\ t_1^2 = \frac{l_1}{l_2}$$

$$= \frac{l_1}{l_1 \times 1{\cdot}000475}$$

$$= \frac{1}{1{\cdot}000475}.$$

$$\therefore\ t_1 = \frac{1}{1{\cdot}000237}.$$

No. of swings per day $= 86400 \times 1{\cdot}000237$

$= 86420{\cdot}48.$

$\therefore$ Gain in time per day $= 86420{\cdot}48 - 86400$

$= 20{\cdot}48$ secs.

The clock gains 20·48 secs. per day.

To show that the expansion of a hollow vessel is the same as if it were solid

We will take the case of a cylindrical vessel.

Let $r =$ radius,

$l =$ length,

$a =$ coefficient of linear expansion.

Periphery of tube at 0° C. $= 2\pi r.$

Periphery of tube at $t°$ C. $= 2\pi r(1 + at).$

$\therefore$ Radius of tube at $t°$ C. $= r(1 + at).$

$\therefore$ Area of cross section of tube at $t°$ C.

$= \pi[r(1 + at)]^2.$

Length of tube at $t°$ C. $= l(1 + at).$

$\therefore$ Volume of tube at $t°$ C. $= \pi[r(1 + at)]^2 \cdot l(1 + at)$

$= \pi r^2 l(1 + at)^3$

$= \pi r^2 l(1 + 3at).$

But $\pi r^2 l =$ volume of tube at 0° C.,

$3a =$ coefficient of cubical expansion of glass.

We have therefore obtained an expression which is applicable to the expansion of a *solid* glass vessel.

EXPANSION OF LIQUIDS

To find the real coefficient of Expansion of a Liquid

I. Dulong and Petit's Method

(See Elementary Notes)

II. Regnault's Method

Two upright tubes, AC, BD, are connected together at the top by a straight horizontal tube of fine bore, AB, and at the bottom by a tube, $CEMNFD$, bent into an inverted **U** near its centre. The upper tube has a small hole bored in its upper surface at K. A connecting tube, G, leading to a receptacle containing compressed air, is attached to the top of the inverted **U**-tube.

Mercury is poured in at A or B, and a sufficient pressure produced in the air chamber to depress the surfaces of the mercury in ME, NF to about the middle of the tubes.

If the mercury in AC and BD is at the same temperature, the surfaces of the mercury in the central tubes will be in the same horizontal plane. If the mercury in AC is at a *higher* temperature than that in BD, the mercury will stand *higher* in NF than in ME.

Let t_1 = temperature of mercury in BD, NF and ME,
D_1 = density of mercury at t_1,
t_2 = temperature of mercury in AC,
D_2 = density of mercury at t_2,
P = *excess* of pressure in air chamber above that of the atmosphere,
$t = t_2 - t_1$,
k = coefficient of expansion of mercury.

Pressure at F = Pressure at D,

$$P + h_1 D_1 = H_1 D_1.$$

$$\therefore\ P = H_1 D_1 - h_1 D_1 \quad \text{.........} (1).$$

Pressure at E = Pressure at C,

$$P + h_2 D_1 = H_2 D_2.$$

$$\therefore\ P = H_2 D_2 - h_2 D_1 \quad \text{.........} (2).$$

From (1) and (2).

$$H_1D_1 - h_1D_1 = H_2D_2 - h_2D_1.$$

$$\therefore\ H_1D_1 - h_1D_1 + h_2D_1 = H_2D_2.$$

$$\therefore\ D_1(H_1 - h_1 + h_2) = H_2D_2.$$

$$\therefore\ \frac{D_1}{D_2} = \frac{H_2}{H_1 - h_1 + h_2}.$$

But

$$\frac{D_1}{D_2} = 1 + kt.$$

$$\therefore\ \frac{H_2}{H_1 - h_1 + h_2} = 1 + kt.$$

$$\therefore\ kt = \frac{H_2}{H_1 - h_1 + h_2} - 1$$

$$= \frac{H_2 - H_1 + h_1 - h_2}{H_1 - h_1 + h_2}.$$

$$\therefore\ k = \frac{H_2 - H_1 + h_1 - h_2}{(H_1 - h_1 + h_2)\,t}$$

$$= \frac{H_2 - H_1 + h_1 - h_2}{(H_1 - h_1 + h_2)(t_2 - t_1)}.$$

Hence find k.

The following points in the experiment should be noted:—

1. The tube, AC, was surrounded by a jacket filled with oil, which could be heated by a fire beneath.

2. The tube, BD, was surrounded by a jacket, through which cold water circulated.

3. A stream of cold water prevented heat from travelling along the mercury in the horizontal tubes, AB and CE.

4. The temperature of the oil in AC was obtained by means of an air thermometer, the bulb of which extended along the whole length.

5. The pressure in the air chamber was increased until mercury began to flow from the hole, K, in AB. The lengths of the vertical columns, H_1 and H_2, were measured from this level.

Advantages of Regnault's method:—

(1) The two surfaces to be compared were brought close together.

(2) They were not surrounded by the jackets, through which it would be difficult to read them.

III. Areometric Method

Take a weighted glass globe, and weigh it in air and in the liquid at two temperatures, t_1 and t_2.

Let $w =$ weight in air,

$w_1 =$ weight in liquid at t_1,

$w_2 =$ weight in liquid at t_2;

$D_1 =$ density of liquid at t_1,

$D_2 =$ density of liquid at t_2,

$t = t_2 - t_1$,

$k =$ coefficient of expansion of liquid.

Wt. of liquid displaced at t_1 $= w - w_1$.

Vol. of liquid displaced at t_1 $= \dfrac{w - w_1}{D_1}$.

Vol. of globe at t_1 $= \dfrac{w - w_1}{D_1}$.

Vol. of globe at t_2 $= \dfrac{w - w_1}{D_1}(1 + 3at)$.

Vol. of liquid displaced at t_2 $= \dfrac{w - w_1}{D_1}(1 + 3at)$ ....(1).

Wt. of liquid displaced at t_2 $= w - w_2$.

We may then follow one of two methods of reasoning :—

1. Vol. of *this* wt. of liquid at $t_1 = \dfrac{w - w_2}{D_1}$.

Vol. of this wt. of liquid at t_2 $= \dfrac{w - w_2}{D_1}(1 + kt)$ ....(2).

But this is the volume of liquid displaced at t_2.

From (1) and (2), $\dfrac{w - w_1}{D_1}(1 + 3at) = \dfrac{w - w_2}{D_1}(1 + kt)$.

$$\therefore\ (w - w_1)(1 + 3at) = (w - w_2)(1 + kt).$$

Hence find k.

2. Vol. of *this* wt. of liquid at $t_2 = \dfrac{w - w_2}{D_2}$ ....(3).

From (1) and (3),

$$\frac{w - w_1}{D_1}(1 + 3at) = \frac{w - w_2}{D_2}.$$

$$\therefore\ \frac{D_1}{D_2}=\frac{w-w_1}{w-w_2}(1+3at).$$

But $$\frac{D_1}{D_2}=(1+kt).$$

$$\therefore\ \frac{w-w_1}{w-w_2}(1+3at)=1+kt.$$

$$\therefore\ (w-w_1)(1+3at)=(w-w_2)(1+kt).$$

Hence find k.

This method was employed by Matthiessen for finding the coefficient of expansion of water.

Note that, if we know k in the above formula, we can find $3a$, i.e. it gives us a method for finding the *coefficient of cubical expansion of a solid.*

Examples

1. A piece of glass, the weight of which in air was 46·76 gms., was found to weigh 31·29 gms. in water at 4° C., its point of maximum density, and 31·51 gms. in water at 60° C. Find the coefficient of expansion of water taking that of glass as ·000027.

Wt. of water displaced at 4° C. = 46·76 − 31·29
= 15·47 gms.

Vol. of water displaced at 4° C. = 15·47 c.c.

Vol. of globe at 4° C. = 15·47 c.c.

Vol. of globe at 60° C. $= 15{\cdot}47\,(1+3at)$
$= 15{\cdot}47\,(1+{\cdot}000027\times 56)$
$= 15{\cdot}47\times 1{\cdot}001512$
= 15·49 c.c.

Vol. of water displaced at 60° C. = 15·49 c.c. ....(1).

Wt. of water displaced at 60° C. = 46·76 − 31·51
= 15·25 gms.

Vol. of *this* wt. of water at 4° C. = 15·25 c.c.

Vol. of this wt. of water at 60° C. $= 15{\cdot}25\,(1+kt)$ ....(2).

But this is the volume of water displaced at 60° C.

From (1) and (2),

$$15{\cdot}49 = 15{\cdot}25\,(1 + kt),$$

$$15{\cdot}49 = 15{\cdot}25\,(1 + 56k),$$

$$15{\cdot}49 = 15{\cdot}25 + (15{\cdot}25 \times 56k),$$

$$(15{\cdot}25 \times 56k) = 15{\cdot}49 - 15{\cdot}25.$$

$$\therefore\ k = \frac{{\cdot}24}{15{\cdot}25 \times 56}$$

$$= {\cdot}000282.$$

Coefficient of expansion of water $= {\cdot}000282$.

2. A glass rod, which weighs 90 gms. in air, is found to weigh 49·6 gms. in a certain liquid at 12° C. At 97° C. its apparent weight in the same liquid is 51·9 gms. Find the coefficient of absolute expansion of the liquid.

Wt. of liquid displaced at 12° C. $= 90 - 49{\cdot}6$

$= 40{\cdot}4$ gms.

Vol. of liquid displaced at 12° C. $= \dfrac{40{\cdot}4}{D_1}$.

Vol. of rod at 12° C. $= \dfrac{40{\cdot}4}{D_1}$.

Vol. of rod at 97° C. $= \dfrac{40{\cdot}4}{D_1}(1 + 3at)$.

Vol. of liquid displaced at 97° C. $= \dfrac{40{\cdot}4}{D_1}(1 + 3at)$..................................(1).

Wt. of liquid displaced at 97° C. $= 90 - 51{\cdot}9$

$= 38{\cdot}1$ gms.

Vol. of *this* wt. of liquid at 97° C. $= \dfrac{38{\cdot}1}{D_2}$ ....(3).

From (1) and (3),

$$\frac{40{\cdot}4}{D_1}(1 + 3at) = \frac{38{\cdot}1}{D_2}.$$

$$\therefore\ \frac{D_1}{D_2} = \frac{40{\cdot}4\,(1 + 3at)}{38{\cdot}1}.$$

But
$$\frac{D_1}{D_2} = 1 + kt.$$

$$\therefore \frac{40{\cdot}4\,(1 + 3at)}{38{\cdot}1} = 1 + kt.$$

$$\therefore\ kt = \frac{40{\cdot}4\,(1 + 3at)}{38{\cdot}1} - 1$$

$$= \frac{40{\cdot}4\,(1 + {\cdot}000027 \times 85)}{38{\cdot}1} - 1$$

$$= \frac{40{\cdot}4\,(1 + {\cdot}002295)}{38{\cdot}1} - 1$$

$$= \frac{(40{\cdot}4 \times 1{\cdot}002295)}{38{\cdot}1} - 1$$

$$= \frac{40{\cdot}49}{38{\cdot}1} - 1$$

$$= \frac{40{\cdot}49 - 38{\cdot}1}{38{\cdot}1}$$

$$= \frac{2{\cdot}39}{38{\cdot}1}.$$

$$\therefore\ k = \frac{2{\cdot}39}{38{\cdot}1 \times 85}$$

$$= {\cdot}000738.$$

Coefficient of expansion of liquid $= {\cdot}000738.$

To find the coefficient of cubical expansion of a solid

1. By weighing it in a liquid at two temperatures, the coefficient of absolute expansion of the liquid being known.

The formula we should use is the one that we have previously obtained,

$$(w - w_1)(1 + 3at) = (w - w_2)(1 + kt).$$

Hence find $3a$.

2. By putting it inside a weight thermometer.

A bar of the substance is introduced into the tube of the thermometer before the neck is drawn out. It is provided with some projections to keep it from lying on the side of the tube, since it is impossible, otherwise, to fill completely the space between the bar and the glass with mercury. The volume and density of the bar at 0° C. must be previously determined. The neck of the thermometer having been drawn out, it is weighed before and after it is filled with mercury. After heating the thermometer it is again weighed and hence the weight of mercury that flows out is determined. The calculation is a long and somewhat complicated one.

EXPANSION OF GASES

Absolute Zero

If we imagine a given mass of gas of which the volume is V_0 and the pressure P_0 at a temperature of 0° C., and imagine the volume kept constant, whilst its temperature is lowered to $-t^\circ$ C., the pressure P_1 by Charles' Law will be given by the formula

$$P_1 = P_0(1 - at),$$

where $a =$ coefficient of expansion of the gas.

If the cooling is continued to a temperature of $\left(\frac{1}{a}\right)$ C.° below 0° C., then

$$P_1 = P_0(1 - 1) = 0,$$

i.e. at this temperature the gas would exert *no pressure* upon the walls of the containing vessel. Now, according to the "Kinetic Theory of Gases," this can only occur when the velocity of translation of the molecules is zero. If, as seems probable, the motion of the atoms in the molecules increases and decreases with the motion of translation of the molecules, it follows that, at a temperature of $-\left(\frac{1}{a}\right)^\circ$ C., the molecules will have completely lost all their motion, both molecular and atomic. Since heat consists of the motion of the molecules, when no such motion exists the body must be devoid of all heat. Since it is impossible to imagine a body colder than one which is devoid of all heat, i.e. one which is at a temperature of $-\left(\frac{1}{a}\right)^\circ$ C., this temperature is called the "Absolute Zero."

Taking a as ·0036625, the mean value for the coefficient of expansion of hydrogen between 0° C. and 100° C., Absolute Zero will be

$$-\frac{1}{\cdot 0036625} = -273^\circ \text{ C.}$$

Although it is impossible to cool a substance down to the Absolute Zero, it is interesting to note that a temperature as low as $-270{\cdot}5^\circ$ C. or $2{\cdot}5^\circ$ A. has been attained by the boiling, under reduced pressure, of liquid helium.

Air Thermometers

I. Jolly's Constant Volume

II. Regnault's Constant Volume

III. Regnault's Constant Pressure

These three types are dealt with in Elementary Notes.

IV. Callendar's Compensated Constant Pressure

In the diagram

A = bulb of air thermometer.

B = tube containing mercury, graduated from the upper end and kept in melting ice.

C = U-tube containing sulphuric acid to act as a pressure gauge.

D = bulb containing dry air, kept in melting ice.

E, F = two similar tubes of which F is a dummy.

G = tap.

The bulb A is connected *directly* with the tube B and *indirectly*, through the gauge C, with the bulb D. Since D is in melting ice, the pressure is constant and it is also *independent of the atmospheric pressure.*

The level of mercury in B is adjusted in each experiment until the gauge shows the pressure in A to be equal to that in D. Errors due to the unknown temperature of the air in E are eliminated by the dummy tube F, since the two tubes are equally affected.

Let A, B and D be placed in melting ice, B *filled with mercury* and the pressure adjusted so that the levels in C are equal. (This must be done by alteration of F or D.) Let the temperature of A rise from T_0° to T_1°. Run mercury out of B, till the pressures in C are again equal. Determine the volume of air expelled from A into B.

Let v_1 = volume of bulb A,

v_2 = volume of air in B, when A is at T_1°.

Note that v_2 will be zero, when the temperature of A is T_0°. The volume that the air, which fills A at T_1°, would occupy at T_0°, would be $v_1 - v_2$. It is important to remember that the air in B is always at T_0°.

Then

$$\frac{v_1 - v_2}{T_0} = \frac{v_1}{T_1},$$

from which T_1 can be found.

Note that v_2 was measured by finding the volume of mercury run out.

Advantages of Callendar's Instrument :—

(1) Alterations in atmospheric pressure no longer come under consideration.

(2) Automatic corrections are made for the connecting tubes.

(3) It is easy to see if the pressure is constant.

(4) Sulphuric acid is more sensitive than mercury.

(5) It is claimed by the inventor that a temperature as high as 450° C. can be measured to within $\frac{1}{10}$ C.° and that the results are very trustworthy.

To find the coefficient of expansion of air by means of a Constant Volume Air Thermometer

We know that $V_2 = V_1(1 + at)$.

It is required to prove that $P_2 = P_1(1 + at)$,

i.e. that the pressure coefficient is the same as the volume coefficient.

This may be done in two ways :—

1. Let V_1 be the volume of a given mass of gas at a temperature $T_1°$ and its pressure P_1.

At *constant pressure* increase the temperature to $T_2°$.

Then the new volume, V_2, is given by the formula

$$V_2 = V_1(1 + at),$$

where a = volume coefficient.

$$\therefore \frac{P_1 V_1}{T_1} = \frac{P_1 V_1 (1 + at)}{T_2} \quad \text{.............................(1).}$$

Then at *constant volume* increase the temperature to $T_2°$.

Then the new pressure, P_2, is given by the formula

$$P_2 = P_1(1 + ct),$$

where c = pressure coefficient.

$$\therefore \frac{P_1 V_1}{T_1} = \frac{P_1 (1 + ct) V_1}{T_2} \quad \text{.............................(2).}$$

From (1) and (2),

$$\frac{P_1 V_1 (1 + at)}{T_2} = \frac{P_1 (1 + ct) V_1}{T_2}.$$

$$\therefore 1 + at = 1 + ct.$$

$$\therefore a = c,$$

i.e. the pressure coefficient is the same as the volume coefficient.

$$\therefore P_2 = P_1(1 + at).$$

2. Let V_1 be the volume of a given mass of gas at 0° C. and its pressure P_1.

At *constant pressure* increase the temperature to t° C. The volume will increase to V_2.

Then $$P_1 V_2 = P_1 [V_1 (1 + at)],$$

where a = volume coefficient.

Then at *constant volume* increase the temperature to t° C. The pressure will increase to P_2.

Then $$P_2 V_1 = [P_1 (1 + ct)] V_1,$$

where c = pressure coefficient.

Now let us apply Boyle's Law to the two states of the gas at t° C.

Then $$P_1 V_2 = P_2 V_1.$$

$$\therefore\ P_1 V_1 (1 + at) = P_1 V_1 (1 + ct).$$

$$\therefore\ 1 + at = 1 + ct.$$

$$\therefore\ a = c,$$

i.e. the pressure coefficient is the same as the volume coefficient.

$$\therefore\ P_2 = P_1 (1 + at).$$

Standard Gas Thermometer

Since the standard thermometric substance employed in all accurate measurements of temperature is either hydrogen or nitrogen, the problem of comparing the readings taken on an ordinary liquid-in-glass thermometer with the gas thermometer is a most important one.

The following is a form of gas thermometer employed at the "Bureau International des Poids et Mesures" at Paris. It consists of two distinct parts:—

1. The bulb containing hydrogen.
2. The manometer, to measure the pressure to which the gas is exposed at the various temperatures.

The bulb, which is elongated in shape and made of platinum iridium, with a capacity of about a litre, is connected by a fine metal tube to the manometer. For the comparison at comparatively low temperatures the bulb and the thermometer, which are to be compared with the gas thermometer, are placed side by side in a long water bath, which is well stirred. For higher temperatures a steam or vapour jacketed vessel is used, similar in principle to the hypsometer. The manometer is combined with a barometer in such a way that, in taking a reading, the height of a single column of mercury only has to be measured.

In the diagram

A = bulb.

T, T = thermometers.

B = metal tube leading to bulb.

C = right-hand limb of **U**-tube attached to B.

D = ivory point to which the level of mercury is adjusted.

E = left-hand limb of **U**-tube, which is open to the atmosphere.

F = flexible steel tube, with tap, supported in a movable cradle, G, and attached to a reservoir, H.

K = barometer tube, supported in a movable cradle, L, the lower end of which dips into the mercury in E.

M = level of mercury in C.

N = level of mercury in E.

P = level of mercury in K.

At each temperature the cradles, G and L, are moved until the mercury is adjusted to D.

Then

$$\begin{aligned}\text{pressure on gas} &= \text{pressure at } M\\ &= \text{atmospheric} + NM\\ &= PN + NM\\ &= PM.\end{aligned}$$

The measurement of the height, PM, is effected by means of a cathetometer, the measurement being facilitated by the fact that the surfaces at P and M are placed vertically one above the other by having a bent barometer tube. The temperature of the mercury column is measured by a series of thermometers attached to the upright.

The readings obtained have to be corrected to allow for the expansion of the bulb on account of rise in temperature and increase in the pressure of the gas inside.

SPECIFIC HEAT

To find the Specific Heat of a Liquid by the Method of Cooling

I. Theoretical

To prove Newton's Law of Cooling.

1. We took a 300 c.c. flask and filled it nearly up to the neck with water at a temperature a little above 60° C. We put it upon a non-conducting stand, stirred the water continually with a thermometer and took the temperature every 2 mins. as it cooled. We took the temperature of the air at the beginning and end of the experiment.

We obtained the following results:—

Mins.	Temp.
0	63·1° C.
2	61·7° C.
4	60·3° C.
6	59·0° C.
8	57·7° C.
10	56·4° C.
12	55·2° C.

We then found the following:—

(1) The fall in temperature in each period of 4 mins.

(2) The average temperature of the water during each period of 4 mins.

(3) The average temperature of the surrounding air during the experiment.

(4) The average difference in temperature between the water and the surrounding air during each period of 4 mins.

(5) The ratio of the fall in temperature during each period of 4 mins. to the average difference in temperature between the water and the surrounding air.

Average temperature of surrounding air = 13° C.

We drew up the following table:—

Period of 4 mins.	Fall in temp. in 4 mins.	Av. temp. of water	Av. diff. in temp.	Test
1st	2·8°	61·7°	48·7°	17·39
2nd	2·6°	59·0°	46·0°	17·69
3rd	2·5°	56·4°	43·4°	17·36

The last column is a test of direct proportion and shows that the fall in temperature in 4 mins. is directly proportional to the average difference in temperature between the water and the surrounding air.

The following results were obtained with a thermometer reading to hundredths of a degree:—

Average temperature of surrounding air = 11·00° C.

Period of 4 mins.	Fall in temp. in 4 mins.	Av. temp. of water	Av. diff. in temp.	Test
1st	1·30°	44·95°	33·95°	26·11
2nd	1·25°	43·70°	32·70°	26·16
3rd	1·20°	42·50°	31·50°	26·26

2. We heated a thermometer to a temperature slightly above 100° C. and allowed it to cool in a calorimeter surrounded by water. Starting from a temperature of exactly 100° C. we took the temperature every half-minute for 3 complete minutes. We took the temperature of the water at the beginning and end of the experiment.

We did the experiment three times and took the mean of our readings, which were very close together.

We obtained the following results:—

Half-mins.	Temp.
0	100° C.
1	77·7° C.
2	61·6° C.
3	50·0° C.
4	41·4° C.
5	35·0° C.
6	30·1° C.

We drew a graph with half-minutes horizontally and temperatures vertically, and obtained a smooth curve, showing that the cooling takes place in a regular manner.

Average temperature of water = 12·3° C.

We then drew up a table as before.

Minute	Fall in temp. in 1 min.	Av. temp. of therm.	Av. diff. in temp.	Test
1st	38·4°	77·7°	65·4°	·59
2nd	20·2°	50·0°	37·7°	·54
3rd	11·3°	35·0°	22·7°	·49

The last column is a test of direct proportion, but it *fails to show* that the fall in temperature in 1 min. is directly proportional to the average difference in temperature between the thermometer and the surrounding air.

Now just as "rate of motion" is measured by finding the distance gone in a given time, so "rate of cooling" is measured by finding the fall in temperature in a given time.

1st Def. Newton's Law of Cooling.

"The rate of cooling of a body is directly proportional to the difference in temperature between it and its surroundings."

Now the quantity of heat given out by a body in a given time can be found as follows:—

Quantity of heat $= m \times s \times (t_1 - t_2)$,

where $m =$ mass of body,

$s =$ specific heat of body,

$t_1 - t_2 =$ fall in temperature.

It is clear from this that the rate of cooling is directly proportional to the quantity of heat given out in a given time, since m and s are constants.

2nd Def. Newton's Law of Cooling.

"The quantity of heat given out by a body in a given time is directly proportional to the difference in temperature between it and its surroundings."

Thus, for a given vessel at a given mean temperature, the quantity of heat given out in a given time is *independent of the nature of the liquid* in the vessel, provided the *volume* of the liquid is the same. This is so as to have the same *area* of heated surface cooling and hence the conditions for cooling the same.

It follows from this that, if we cool two liquids, of mass m_1 and m_2, having different specific heats s_1 and s_2, in the same vessel, through the same range of temperature $(t_1 - t_2)$, *they will give out heat at the same rate*, since they will have the same mean temperature during cooling, i.e. *the quantity of heat given out in unit time will be the same.*

Heat given out by one liquid $= m_1 \times s_1 \times (t_1 - t_2)$,

Heat given out by other liquid $= m_2 \times s_2 \times (t_1 - t_2)$.

Let θ_1, θ_2 = time taken, respectively.

$$\text{Heat given out in unit time by one liquid} = \frac{m_1 \times s_1 \times (t_1 - t_2)}{\theta_1}.$$

$$\text{Heat given out in unit time by other liquid} = \frac{m_2 \times s_2 \times (t_1 - t_2)}{\theta_2}.$$

But these are equal,

$$\therefore \frac{m_1 \times s_1 \times (t_1 - t_2)}{\theta_1} = \frac{m_2 \times s_2 \times (t_1 - t_2)}{\theta_2},$$

$$\therefore \frac{m_1 \times s_1}{\theta_1} = \frac{m_2 \times s_2}{\theta_2}.$$

II. Experimental

To find the specific heat of turpentine.

We took an apparatus consisting of the following parts:—

(1) Small calorimeter, lamp-blacked on the *outside*, with lid, containing thermometer and stirrer.

(2) Larger calorimeter, lamp-blacked on the *inside*, containing air. (A vacuum would be preferable.)

(3) Largest calorimeter, containing ice and calorimeter (2).

We found the time, θ_1, taken by a mass, m_1, of water to fall from t_1 to t_2, the water being well stirred. We then found the time, θ_2, taken by a mass, m_2, of turpentine to fall from t_1 to t_2, the *volume* of the turpentine being equal to that of the water.

We obtained the following results:—

$$\begin{aligned} m_1 &= 25{\cdot}00 \text{ gms.} \\ \theta_1 &= 7 \text{ mins. } 58 \text{ secs.} \\ &= 478 \text{ secs.} \\ m_2 &= 21{\cdot}75 \text{ gms.} \\ \theta_2 &= 3 \text{ mins. } 35 \text{ secs.} \\ &= 183 \text{ secs.} \\ t_1 - t_2 &= 52{\cdot}0^\circ \text{ C.} - 32{\cdot}0^\circ \text{ C.} \\ &= 20 \text{ C}^\circ. \end{aligned}$$

We have seen that

$$\frac{m_1 \times s_1}{\theta_1} = \frac{m_2 \times s_2}{\theta_2}.$$

$$\begin{aligned} \therefore s_2 &= \frac{m_1 \times s_1}{\theta_1} \times \frac{\theta_2}{m_2} \\ &= \frac{25 \times 1 \times 183}{478 \times 21{\cdot}75} \\ &= {\cdot}436. \end{aligned}$$

Specific heat of turpentine.

By experiment = ·436.
By book = ·41.

LATENT HEAT

Total Heat of Steam

Def. "The total heat of steam at $t°$ C. is the quantity of heat required to turn 1 gm. of water, *initially at* 0° C., into steam at $t°$ C."

It can be shown by experiment that the temperature at which water boils depends upon the pressure. Therefore, to make water boil at different temperatures, the pressure must be suitably modified.

Regnault made experiments to determine the total heat of steam. Before his time two views had been held:—

1. Watt had stated that the total heat of steam was constant.

∴ At higher temperatures the latent heat of steam would be *less*, i.e. the latent heat would diminish by 1 for each rise in temperature of 1 C.°

2. Creighton and Southern had stated that the latent heat of steam was constant.

∴ At higher temperatures the total heat of steam would be *more*, i.e. the total heat would increase by 1 for each rise in temperature of 1 C.°

Regnault showed that *neither* of these views was correct.

Regnault's Method for finding the total heat of Steam

The water was heated in a boiler and the vapour formed passed down through the liquid, as in Berthelot's Method for finding the latent heat of steam, and was conveyed to the calorimeter by a carefully-jacketed tube. The vapour entered the upper of two copper spheres, passed into the lower one and then passed upwards through a copper worm. The water, which condensed in the worm and spheres, ran into the lower sphere, and was drawn off and weighed. The upper end of the worm was connected to an open mercury manometer, by means of which the pressure could be varied. He employed pressures between ·2 and 13·6 atmos.

Let $Q =$ total heat of steam at $t°$ C.,

$L =$ latent heat of steam at $t°$ C.

He found that

$$Q = 606{\cdot}5 + {\cdot}305t.$$

This shows that the total heat of steam *increases* with temperature.

Again
$$Q = t + L.$$
$$\therefore\ L = Q - t$$
$$= (606{\cdot}5 + {\cdot}305t) - t$$
$$= 606{\cdot}5 - {\cdot}695t.$$

This shows that the latent heat of steam *decreases* with temperature.

To find the value of Q at 100° C.

$$Q = 606{\cdot}5 + {\cdot}305t$$
$$= 606{\cdot}5 + ({\cdot}305 \times 100)$$
$$= 606{\cdot}5 + 30{\cdot}5$$
$$= 637.$$

To find the value of L at 100° C.

$$L = 606{\cdot}5 - {\cdot}695t$$
$$= 606{\cdot}5 - ({\cdot}695 \times 100)$$
$$= 606{\cdot}5 - 69{\cdot}5$$
$$= 537.$$

To find the temperature at which the latent heat of steam is zero.

Since $L = 606{\cdot}5 - {\cdot}695t$, for L to be zero, we must have

$$606{\cdot}5 - {\cdot}695t = 0.$$
$$\therefore\ {\cdot}695t = 606{\cdot}5.$$
$$\therefore\ t = \frac{606{\cdot}5}{{\cdot}695}$$
$$= 872{\cdot}8^\circ\,\text{C}.$$
$$\text{Temperature} = 872{\cdot}8^\circ\,\text{C}.$$

Errors in Regnault's work :—

(1) His thermometry was imperfect.

(2) The variation in the specific heat of water between 0° C. and 60° C. was unknown to him.

(3) He admitted that the observations below 175° C. were vitiated by an escape of steam into the idle calorimeter. (He used two calorimeters to get rid of radiation errors.)

Steam Calorimeters

The specific heat of a solid can be determined in terms of the latent heat of steam. For this purpose a steam calorimeter is used. It consists of a glass vessel with a metal top, through which pass three tubes. Two of these, A and B, are wide for the entrance and exit of steam. The third, C, is a narrow one, lined with Plaster of Paris, through which a fine wire, attached to the short pan of a balance, can pass. The wire carries a metal tray. On passing dry steam into the calorimeter the temperature of the tray rises to that of the steam and steam is condensed upon it, 1 gm. being condensed for every 536 cals. absorbed by the tray. The gain in weight of the tray is measured.

To find the specific heat of copper

We filled the tray full of pieces of copper and passed in steam until the tray ceased to gain in weight. We found the gain in weight of the tray. We obtained the following results:—

Weight of copper (1) = 46·17 gms.
Weight of copper (2) = 46·81 gms.
Temp. of copper (1) = 17° C.
Temp. of copper (2) = 100° C.

$$\text{Weight of steam condensed} = 46{\cdot}81 - 46{\cdot}17 = {\cdot}64 \text{ gm.}$$

1 gm. of steam in condensing gives out 536 cals.

·64 gm. of steam in condensing gives out $536 \times {\cdot}64 = 343{\cdot}04$ cals.

∴ Heat given out by steam in condensing = 343·04 cals.

This heat has gone into the copper.

$$\text{Rise in temp. of copper} = 100 - 17 = 83 \text{ C.}^\circ$$

To raise 46·17 gms. of copper 83 C.° requires 343·04 cals.

$$\text{To raise 1 gm. of copper 1 C.}^\circ \text{ requires } \frac{343{\cdot}04}{46{\cdot}17 \times 83} = {\cdot}089 \text{ cal.}$$

Specific heat of copper = ·089.

The practical difficulties in the experiment are as follows:—

(1) To prevent the wire rubbing against the sides of the hole.

(2) To prevent steam condensing upon the wire. This difficulty was overcome by Joly's apparatus.

To find the Specific Heat of a Gas at Constant Volume by Joly's Differential Steam Calorimeter

In the diagram

B = balance.

W, W = fine platinum wires.

C, C = two thin copper spheres.

S = steam chamber.

E, E = wires heated by electricity.

T, T = trays beneath spheres to catch condensed steam.

The thermal capacities of the two spheres are equal, so that, if they are in equilibrium to begin with, they will remain in equilibrium when steam is passed in, since equal masses of water will be condensed on each sphere. Fill one sphere with the gas *under pressure,* the other being *vacuous.* Find the mass of the gas by weighing. Take the temperature of S when it is constant. Then pass in dry steam and find the *difference* in the mass of water condensed on the two spheres. Since the thermal capacities of the two spheres are equal, this difference must be due to the *heat absorbed by the gas.* The volume of the gas remains very nearly constant.

The data obtained will be as follows:—

Weight of gas taken.

Temp. of gas (1).

Difference in weight of steam condensed on the two spheres.

From these data the specific heat of the gas at constant volume can be obtained.

The practical difficulties in the experiment are as follows:—

The apertures in the steam chamber, through which the fine platinum wires passed, were the main sources of difficulty:—

(1) If large, steam escaped.

(2) If small, drops of water condensed on the wires.

The method employed was to make the holes in Plaster of Paris, which, being an absorbent substance, prevented the formation of drops. Small coils of platinum wire also surrounded the wires just above the holes and these were rendered hot by the passage of an electric current.

CONDUCTION OF HEAT

To prove that

$$\frac{k_1}{k_2} = \frac{l_1^2}{l_2^2}.$$

Let AB, CD be two bars, of which the temperature gradients are known. They must be sufficiently long for the far ends to be at the temperature of the room.

Let t_1 = temperature of A and C,

t_2 = temperature of E and F.

We shall suppose that AE is twice CF. Then for any other two temperatures we shall have the length on AB twice as long as the length on CD. This will be the case, for instance, for lengths whose end temperature is that of the room.

Let us suppose that the bars have the same area of cross section and that their surfaces are in the same state. Now the amount of heat radiated from a bar is proportional to the product of the area exposed and the mean difference in temperature between the bar and its surroundings. Since for every cm. of AB at a certain mean temperature above that of the room there is a half cm. of CD at the same mean temperature, the heat radiated from AB in a given time will be *twice* that radiated from CD.

Quantity of heat radiated in one case = 2 × quantity of heat radiated in other case.

∴ Quantity of heat crossing a section of the rod AB at A = 2 × quantity of heat crossing a similar section of the rod CD at C.

In the same way the quantity of heat crossing any section of AB at any temperature is twice the quantity of heat crossing a similar section of CD, which is at the same temperature.

Again, the temperature gradient at any point on AB is *half* the temperature gradient at a point having the same temperature on CD.

Suppose we take a small element, M, of AB and a similar element, N, of CD, at the same temperature.

Let Q_1 = quantity of heat crossing M in 1 sec.

Q_2 = quantity of heat crossing N in 1 sec.

G_1 = temperature gradient at M.

G_2 = temperature gradient at N.

Then

$$Q_1 = k_1 ATG_1,$$

$$Q_2 = k_2 ATG_2,$$

$$\therefore \frac{Q_1}{Q_2} = \frac{k_1 G_1}{k_2 G_2},$$

$$\therefore \frac{k_1}{k_2} = \frac{Q_1 G_2}{Q_2 G_1}.$$

But we have seen that

$$Q_1 = 2Q_2,$$

$$G_2 = 2G_1,$$

$$\therefore \frac{k_1}{k_2} = \frac{2Q_2 2G_1}{Q_2 G_1}$$

$$= 4$$

$$= 2^2$$

$$= \left(\frac{l_1}{l_2}\right)^2$$

$$= \frac{l_1^2}{l_2^2},$$

$$\therefore \frac{k_1}{k_2} = \frac{l_1^2}{l_2^2}.$$

This proof may be made a general one; e.g. if the length on one bar is n times that on the other,

$$Q_1 = nQ_2,$$

$$G_2 = nG_1.$$

Then

$$\frac{k_1}{k_2} = \frac{Q_1 G_2}{Q_2 G_1}$$

$$= \frac{nQ_2 nG_1}{Q_2 G_1}$$

$$= n^2$$

$$= \left(\frac{l_1}{l_2}\right)^2$$

$$= \frac{l_1^2}{l_2^2},$$

$$\therefore \frac{k_1}{k_2} = \frac{l_1^2}{l_2^2}.$$

To prove that

$$\frac{k_1}{k_2}=\frac{G_2^2}{G_1^2}.$$

Let l_1, l_2 = lengths having same end temperatures.

Then
$$G_1=\frac{D}{l_1},$$
$$G_2=\frac{D}{l_2},$$
$$\therefore \frac{G_1}{G_2}=\frac{l_2}{l_1},$$
$$\therefore \frac{l_1}{l_2}=\frac{G_2}{G_1}.$$

But
$$\frac{k_1}{k_2}=\frac{l_1^2}{l_2^2}$$
$$=\frac{G_2^2}{G_1^2},$$
$$\therefore \frac{k_1}{k_2}=\frac{G_2^2}{G_1^2}.$$

Diffusivity

We took two cylinders, one of iron and the other of bismuth, of the same dimensions. We placed a piece of paraffin wax on each and put them together on a copper plate, heated by a bunsen burner. We found that the wax on the bismuth *began* to melt before that on the iron, but that the wax on the iron was *completely* melted before that on the bismuth.

Substance	Conductivity	Specific heat
Iron	·166	·113
Bismuth	·017	·030

The experiment and these numbers show that the rate at which heat is conducted along a bar in the variable state is *not* dependent upon the conductivity *alone.* It depends also upon the specific heat of the substance or rather upon the "thermal capacity of unit volume." The term "diffusivity" is used in this connection.

Def. "Diffusivity is the rise in temperature produced in a layer of unit thickness by the heat transmitted in unit time through a similar layer of unit thickness having unit difference of temperature between its faces."

Let $Q =$ quantity of heat transmitted,
$k =$ conductivity,
$f =$ diffusivity,
$s =$ specific heat,
$d =$ density.

Then
$$Q = \frac{kATD}{B}$$
$$= kA,$$
since T, D and B are all unity.

Thermal capacity of layer $=$ specific heat × mass
$=$ specific heat × volume × density
$= sAd.$

Then rise in temperature
$$= \frac{\text{quantity of heat}}{\text{thermal capacity of layer}}$$
$$= \frac{kA}{sAd}$$
$$= \frac{k}{sd}.$$
$$\therefore f = \frac{k}{sd},$$
i.e. diffusivity varies directly as conductivity and inversely as specific heat and density. Hence at the beginning of experiments on conductivity the temperature near the source rises more quickly on bars of low specific heat and density than on bars of high specific heat and density, other things being equal.

It should be noted that
$$sd = \text{thermal capacity of unit volume.}$$

Determination of the Thermal Conductivity of a Solid by Forbes' Method

If one end of a bar is heated until it reaches the stationary state, the heat that passes in 1 sec. through a section 1 cm. in thickness in any part of the bar is equal to the heat lost by radiation from the part of the bar beyond this section in 1 sec. This is neglecting the heat given off from the surface of the section, which will be small compared with that given off by the surface of the bar beyond the section, if the bar is long.

The experiment was divided into two parts:—

1. Statical experiment.

The temperature of each point on the bar is stationary.

2. Dynamical experiment.

The temperature of each point on the bar is the same, but is varying throughout the experiment.

1. Statical experiment.

The end of the bar was heated by being inserted in a crucible full of fused solder, which was maintained at a constant temperature. Small holes, made in the upper surface of the bar, held thermometers, the bulbs being surrounded by mercury. When the stationary state was reached, a curve was drawn connecting the length of the bar and the temperature, from which the fall in temperature per cm. length could be ascertained at any point.

2. Dynamical experiment.

The same bar was heated uniformly throughout its length and allowed to cool, the rate of cooling being determined for various temperatures; i.e. the time taken to fall through a certain temperature. The quantity of heat given out by the bar during a given interval of time, in which the temperatures fell by a certain number of degrees, was calculated.

Heat given out by bar in a given interval of time when at a known *mean* temperature

$$= \text{mass of bar} \times \text{specific heat} \times \text{fall in temperature}.$$

From this the heat given out by *unit* length of the bar in 1 sec. for a given *mean* temperature was calculated.

A second curve was drawn showing the relation between the heat given out by unit length of the bar in 1 sec. and various mean temperatures.

Now from the first curve the mean temperature of the bar beyond the section could be calculated and the heat given out per sec. by this length of the bar for this *mean* temperature could be obtained by aid of the second curve. But this quantity of heat has passed through the given section in 1 sec. Knowing the area of this section and the difference in temperature between its ends from the first curve, we can find k, for

$$k = \frac{QB}{ATD}.$$

Of these, all are easy to find except Q, which is obtained by the aid of the dynamical experiment.

Determination of the Thermal Conductivity of a Liquid

I. Despretz' Method

A cylindrical wooden vessel, *B*, about a metre long, was furnished with a number of apertures down one side, into which thermometers were inserted. The vessel was filled with the liquid to be examined, which was allowed to acquire a uniform temperature. Hot water was then poured on to a shallow copper vessel, *A*, at the top of the cylinder and the hot water was renewed every 5 mins. A temperature curve was obtained just as in the case of a metal bar. A permanent state was reached after 30 or 40 hours.

The conductivities for various liquids were proportional to the squares of the distances downwards from the copper vessel corresponding to a given fall in temperature.

II. Bottomley's Method

He modified Despretz' Method by having *two* thermometers placed horizontally one above the other at a small distance apart to determine the fall in temperature per cm. length near the top. The *mean* temperature of the water below that point was indicated by a *thermometer with a long bulb placed vertically.* From successive readings of this thermometer the quantity of heat which passed through the section near the top of the cylinder in 1 sec. could be calculated. The vessel *A* was dispensed with, hot water being poured in a slow stream on to a small wooden float and withdrawn later through a suitable aperture.

He calculated the conductivity thus :—

$$\text{Conductivity} = \frac{\text{heat passing through unit area in 1 sec.}}{\text{fall in temperature per cm. at section}}.$$

Since

$$Q = \frac{kATD}{B},$$

$$k = \frac{QB}{ATD}$$

$$= \frac{Q}{D},$$

since B, A and T are unity.

This method was unlike the others in being *a variable and not a permanent state method.*

Determination of the Thermal Conductivity of a Gas

The method employed is to determine *the rate of cooling* of a thermometer bulb, first in a vacuum and then in the gas. In order to eliminate convection currents the pressure of the gas is reduced. The conductivity is independent of the pressure of the gas, unless this is very small. When the later stages of exhaustion are reached, *a sudden fall in conductivity takes place.* This explains the effectiveness of "Dewar's vacuum vessel."

RADIATION OF HEAT

Prévost's Theory of Exchanges

The question that the Theory deals with is this:—

"Does the radiation from a body depend only upon the body itself or also upon the bodies which surround it?"

Foundation for the Theory of Exchanges

If an enclosure is maintained at a constant temperature and we put a thermometer inside it, we might describe what occurs in the following manner:—

1. If the thermometer is at a *lower* temperature, it will receive energy from the surrounding walls by radiation.

2. If it is at a *higher* temperature, it will give out energy, until, in either case, it arrives at the temperature of the enclosure, after which everything remains steady.

But this is probably not a complete account of what takes place, for, according to the kinetic theory of matter, the molecules of the enclosure and of the thermometer are still in a state of vibration, i.e. still in a condition to send out radiation.

We therefore conclude that the radiation is going on just as before and that the *apparent* cessation of transfer is due to a *balance of exchange*, the thermometer absorbing just as much radiation as it is giving out. The space between the two bodies is the medium of two equal and opposite streams of radiation. We may suppose that there is *a total radiation from a body, depending on its nature and temperature alone and not on the nature and temperature of the surrounding bodies.* When a body ceases to lose or gain energy, it is receiving an amount equal to its own radiation.

We imagine a process *more complex* than that for which we have direct experimental evidence. We may illustrate this by considering the case of two commercial firms, which have many transactions in both directions throughout the year, but no balance, or only a small one, at the end.

Statement of the Theory of Exchanges

It was stated in 1792 by Prévost of Geneva:—

Def. "Every body emits radiation in all directions at a rate which depends *only* upon the nature and temperature of its surfaces and *not* upon the nature or temperature of surrounding bodies."

At the same time it absorbs a certain fraction of the radiation it receives from other bodies and this fraction is a measure of the "absorbing power" of its surface for a particular kind of radiation.

Experiments to illustrate the Theory of Exchanges

1. Place a block of ice in the focus of one of a pair of conjugate mirrors and a thermometer in the focus of the other. The temperature of the thermometer falls.

2. Place a thermometer in a cavity in a block of ice in such a way that it does not touch the ice. The temperature of the thermometer falls.

3. Place a block of ice at a short distance from one of the *blackened* bulbs of a differential air thermometer, the other being surrounded by a tin can. The temperature of the exposed bulb falls.

The explanation in all these cases is as follows:—

The ice *screens* the thermometer from the radiation emitted by surrounding bodies, so that more energy is radiated from the bulb than is received by it. Consequently the temperature of the bulb falls.

These experiments all support Prévost's Theory, that the thermometer is continually giving out heat, its final temperature depending upon the amount it receives *from other bodies.*

Applications of the Theory of Exchanges

1. Relation between Absorbing and Radiating Powers.

If a body absorbs any kind of radiation, it must also emit the same kind at the same temperature and, if it is placed in a "uniform temperature enclosure," emission will be equal to absorption.

Def. "A uniform temperature enclosure is one in which the bodies are entirely surrounded by bodies at their own temperature."

Imagine two silver surfaces, one polished and the other lamp-blacked, placed in the same enclosure. They will maintain the same temperature.

Now polished silver is a good reflector and therefore a bad absorber. It must also be a bad radiator or its temperature would *fall.*

Lamp-black, on the other hand, is a good absorber. It must also be a good radiator or its temperature would *rise.*

This shows that good absorbers are good radiators and *vice versa.*

If we have two surfaces, A and B, it follows that, if they remain at the same temperature,

$$\frac{\text{Absorbing power of } A}{\text{Absorbing power of } B} = \frac{\text{Radiating power of } A}{\text{Radiating power of } B}.$$

2. Condition prevailing in a uniform temperature enclosure.

A body placed in a uniform temperature enclosure finally comes to the temperature of the enclosure. When this state is reached, on the Theory of Exchanges, the body is receiving everywhere just as much heat as it radiates. Since it is giving out radiation equally at all points of its surface, it is receiving the same total quantity at all points, and, since the surface of the body points in different directions, it follows that the different parts of the enclosure must all be giving out radiation equally. The radiation is therefore *independent of the nature of the enclosure.*

Imagine a hollow iron ball coated inside partly with the following substances:—

(1) Lamp-black.

(2) Polished silver.

(3) Rock salt.

Let it be heated red hot and kept at a constant temperature. There is the total or full radiation for the temperature from everything, and everything will appear the same *colour*, since it is not only the same *quantity* of radiation, but also the same *quality*, that is being given out.

(1) Lamp-black radiates much, but reflects little.

(2) Polished silver radiates little but reflects much.

(3) Rock salt is transparent to the radiation from the iron behind and reflects enough to make up the full radiation.

(4) The uncovered iron partly reflects and partly radiates.

The result is *one uniform glare* and it would be impossible to see the boundary lines between the different substances. This is unobtainable in a light room, since the sun, from which the light comes, is outside the enclosure and at a much higher temperature. It can, however, be obtained to a certain extent in the cavities of a hot fire. If pieces of coloured glass are put in, they become indistinguishable, each restoring to the stream what it takes from it; e.g., if a piece of coloured glass absorbs the red rays from the full radiation, it will also give out red rays.

3. To prove that the emissive and absorptive powers of a body are equal.

Def. "The absorptive power of a *body* is the fraction of the radiant energy incident upon it, which the body is able to absorb."

It has been found by experiment that a surface covered with lamp-black is capable of absorbing practically all the *heat* radiation which falls upon it and hence its absorptive power is unity. It is obvious that, since a body cannot absorb more heat than is incident upon it, no body can possess an absorptive power greater than unity. A body whose absorptive power is unity is called a "perfectly black body."

The incident radiation, which is not absorbed by a body, is *reflected*, provided that the body is opaque. Thus, if a quantity, E, of radiant energy is incident upon a surface of which the absorptive power is a, the quantity of energy absorbed is Ea and the quantity reflected is $E(1-a)$.

Def. "The emissive power of a *body* is the ratio of the quantity of radiant energy emitted by 1 sq. cm. of its surface, under given conditions, to the quantity emitted under the same conditions by 1 sq. cm. of a body of which the *absorptive power* is unity, i.e. of a perfectly black body."

Suppose we have a body A, of which the absorptive power is unity. *Its emissive power will also be unity, since, if it were not, its temperature would rise.* Let it be placed in an enclosure the walls of which have the following properties:—

$a =$ absorptive power,

$e =$ emissive power,

$S =$ area of surface.

Let the temperature become *the same throughout*, so that, according to Prévost's Theory of Exchanges, the quantity of heat radiated by the body A is equal to the heat received from the enclosure.

Let us suppose that A loses E units of heat by radiation per sec. Then the walls will absorb Ea units and reflect $E(1-a)$ units per sec. This heat reflected from the enclosure will be completely absorbed by A, *since its absorptive power is unity.* Hence in 1 sec. the body A will lose a quantity of heat equal to

$$\begin{aligned} & E - E(1-a) \\ & = E - E + Ea \\ & = Ea. \end{aligned}$$

But, since its temperature remains constant, this means that the enclosure must have radiated Ea units per sec., which are absorbed by A. Now, since the area of the enclosure is S, the radiation per sq. cm. is $\frac{Ea}{S}$. If, however, the enclosure had been perfectly black, it would have absorbed E and radiated E. Hence the heat emitted per sq. cm. would have been $\frac{E}{S}$.

Now the emissive power, e, is the ratio of the *actual* emission to the emission, under the same conditions, of a perfectly black body.

$$\begin{aligned} \therefore e &= \frac{Ea}{S} \div \frac{E}{S} \\ &= a. \end{aligned}$$

Emissive power = absorptive power.

Note that for the terms "emissive power" and "absorptive power" are also used the terms "coefficient of emission" and "coefficient of absorption," though the former terms are used of a *body* and the latter of a *substance.*

4. To prove experimentally that the coefficients of absorption and emission for a given substance are equal.

The apparatus was devised by Ritchie. Two hollow metal drums, B and C, are filled with air and are connected by a glass tube, which is partly filled with some liquid, such as sulphuric acid, to act as an indicator, as in a differential air thermometer. A third drum, A, placed between them, can be filled with hot water. The faces of B and A, turned towards the right, are coated with lamp-black and the faces of A and C, turned towards the left, are coated with silver foil.

When hot water was placed in A, it was found that the liquid in the glass tube did not move, showing that the drums, B and C, were receiving the same amount of heat from A.

Now the lamp-black surface of B absorbs the heat emitted by the silver surface of A, and the silver surface of C absorbs the heat emitted by the lamp-black surface of A.

Since the heat received is the same, it shows that, although the quantity of heat emitted by the silver surface is small, yet, since the lamp-black absorbs all the heat, the result is the same as when the large amount of heat radiated by the lamp-black surface falls on the silver surface, for in this case only a small proportion of the incident heat is absorbed.

ISOTHERMALS

The relation between the volume and pressure of a given mass of gas at constant temperature is stated in Boyle's Law.

Def. Boyle's Law.

"The volume of a given mass of gas at constant temperature is inversely proportional to the pressure."

This relation can be represented by a graph, which is a rectangular hyperbola and is called an "isothermal" for the gas, since it is "at constant temperature."

We may note, here, that no gas exactly obeys Boyle's Law.

See the work of

1. Regnault.
2. Amagat.

A "Perfect Gas" is one that would obey Boyle's Law exactly.

There are two ways in which Boyle's Law results may be plotted :—

(1) V horizontally, P vertically,

(2) P horizontally, PV vertically.

If Boyle's Law were exactly true, the latter would give a *horizontal* line. If the line went *up*, it would mean that the volume was decreasing *less* than it should do according to Boyle's Law. If the line went *down*, it would mean that the volume was decreasing *more* than it should do according to Boyle's Law.

The relation between the volume and temperature of a given mass of gas at constant pressure is stated in Charles' Law.

Def. Charles' Law.

"The volume of a given mass of gas at constant pressure is directly proportional to the absolute temperature."

Thus, if the temperature rises, the volume will become greater.

We can therefore find the volume which a given mass of air will occupy when at a temperature of

(1) Melting ice,

(2) Steam.

Thus suppose $ABCD$ is the isothermal for 0° C. At a pressure of 20 atmos. the volume is represented by the point C. If the temperature is now raised to 100° C., the volume will increase to G, and by Boyle's Law we can get a fresh curve $EFGH$, which is the isothermal for this temperature.

If we divided the distance CG into 100 equal parts, we could draw a hundred isothermals in this way.

CONTINUITY OF STATE

Boyle's Law at High Pressures

If we desire to test the accuracy of Boyle's Law at high pressures, a difficulty at once presents itself, for, as the pressure increases, the volume decreases and therefore the accuracy with which the volume of the gas can be determined is diminished.

For instance, if we start with 100 c.c. of gas and the error in estimating the position of the mercury meniscus is ·1 c.c., the error is ·1 °/ₒ. If we halve the volume, we shall get the *same* error, but it will now be ·2 °/ₒ.

This difficulty was overcome by

1. Regnault,
2. Amagat.

I. Regnault's Experiments

He kept the volume of the gas on which he was experimenting *large* by using

1. A mercury pump for increasing the pressure, with an open-air manometer.
2. An air pump for increasing the volume of the gas after each compression.

Thus, if he started with a volume V_1 at atmospheric pressure P_1, he halved the volume and found the pressure P_2 required to do this. Then he *pumped in air* till the volume was once more V_1 and *the pressure was still* P_2. He once more halved the volume and found the pressure required to do this. He then continued this process.

Now, since the volume in each case is double what it was in the preceding case *at the same pressure*, to test PV we must divide the product in each case by 1, 2, 4, 8, etc. respectively.

Regnault obtained the following results:—

(1) No gas obeys Boyle's Law exactly.

(2) For most gases the product PV *decreases* as P is increased.

(3) For hydrogen the product PV *increases* as P is increased.

II. Amagat's Experiments

He used the same method as Regnault, only that he had a longer manometer, about 200 ft long, and so obtained higher pressures. He also made experiments at different temperatures.

Amagat obtained the following results:—

He drew curves connecting PV and P, with PV vertically and P horizontally.

(1) Nitrogen and most other gases.

The curves at first go down, then are nearly horizontal and afterwards go up.

(2) Hydrogen.

The curves go up. It has been found, however, that *at low temperatures* the curves are similar to those of Nitrogen, i.e. they go down at first.

(3) Carbon Dioxide.

The curves resemble those of nitrogen *at high temperatures*, but *at low temperatures* the minimum points on the curves are greatly exaggerated, giving a V-shaped effect.

Amagat's results are usually expressed in the following manner:—

P_0 = 1st pressure in mm. of mercury.
V_0 = 1st volume.
P_1 = pressure required to halve V_0.

Nitrogen		Hydrogen		Carbon Dioxide	
P_0	$\frac{P_0V_0}{P_1V_1}$	P_0	$\frac{P_0V_0}{P_1V_1}$	P_0	$\frac{P_0V_0}{P_1V_1}$
753·96	1·001012	2211·18	·998584	764·03	1·007597
1159·43	1·001074	3989·47	·996961	1414·77	1·012313
2159·22	1·001097	5845·18	·996121	2164·81	1·018973
3030·22	1·001950	7074·96	·994697	3186·13	1·028494

Andrews' Experiments on Carbon Dioxide

Andrews, in 1863, employed an apparatus consisting of the following parts:—

1. Two tubes, one containing air and the other carbon dioxide, the gas in each case being enclosed by means of a pellet of mercury.

2. Two strong copper cylinders in which the tubes were firmly fixed, with the upper parts projecting. There was communication between the copper cylinders by means of a cross tube. The cylinders were filled with water and pressure was produced by means of plungers, which affected both tubes equally. The volumes were read by observing the position of the mercury surfaces and the pressures by applying Boyle's Law to the air in one of the tubes.

3. A rectangular brass case, closed before and behind with plate-glass, surrounded each capillary tube and allowed it to be maintained at any required temperature.

He drew a number of isothermals with P vertically and V horizontally.

The nature of the isothermals was as follows:—

(1) At 13·1° C., starting from the right, the isothermal first obeys Boyle's Law, but, when a pressure of 50 atmos. is reached, a discontinuity occurs and it becomes horizontal. At this point he observed that liquefaction took place. The pressure then remained constant till all the gas was liquefied, i.e. it was impossible to increase the pressure, since the gas kept liquefying. Then further increase in pressure caused only a slight alteration in volume, since a liquid is almost incompressible, and the isothermal became almost vertical.

(2) At 21·5° C. similar characteristics are observed, only that liquefaction does not take place till 61 atmos. and the horizontal part is shorter.

(3) At 31·1° C. the discontinuity is no longer observed and liquefaction does not take place, even when the pressure is 100 atmos.

It follows from this that above 30·92° C. liquefaction cannot take place, however great the pressure may be. This temperature is called the "critical temperature" for carbon dioxide.

Def. "The critical temperature of a substance is the temperature above which liquefaction cannot take place."

All gases have a critical temperature.

Typical Form of Isothermals

The isothermals of a substance, which cannot exist in a solid condition at ordinary temperatures and pressures, are shown in the diagram.

We may distinguish between four distinct areas:—

1. Unsaturated vapour.
2. Liquid and saturated vapour.
3. Liquid.
4. Gas.

Andrews suggested that the term "gas" should be restricted to the condition of a substance above the critical point.

The vertex of the dotted curve is called the "critical point." It represents three things:—

(1) A temperature of 30·92° C., the "critical temperature."

(2) A pressure of 73 to 75 atmos., the "critical pressure."

(3) A volume, which is the "critical volume" and is stated as the *volume of unit mass.*

Def. "The critical pressure of a substance is the pressure below which it is impossible to liquefy it *at its critical temperature.*"

Cagniard de la Tour's Experiment

Cagniard de la Tour, in 1822, took a tube as shown in the diagram, where

A = air,
B = mercury,
C = alcohol or alcohol vapour.

We may note the following points about the experiment:—

1. The air in A served to indicate the pressure.

2. When the whole was heated, the volume of the alcohol remained practically constant and the pressure increased.

3. The surface of the liquid gradually became less concave, showing that the surface tension was diminishing.

4. When 225° C. was reached, the surface suddenly disappeared, so that the space above the mercury was filled with a homogeneous vapour, the two states appearing to meet.

5. The pressure, when this occurred, was 129 atmos.

6. He obtained similar results with ether, naphtha, etc.

As the temperature is raised, the vapour becomes more and more dense, through increased evaporation, whilst the liquid expands, becoming less and less dense, so that the properties of the two gradually approach one another.

Drion has shown that the coefficients of expansion of these liquids increase rapidly with temperature, becoming 2, 3 or even 4 times greater than that of air.

We may also note the following points:—

(1) The temperature 225° C. is the critical temperature for alcohol.

(2) When the critical point is reached, the latent heat of vaporisation is *nil*, the liquid and gaseous states being identical. See "Total Heat of Steam," where we found that

$$Q = 606{\cdot}5 + {\cdot}305t.$$

But

$$Q = t + L.$$

$$\begin{aligned} \therefore\ L &= Q - t \\ &= 606{\cdot}5 + {\cdot}305t - t \\ &= 606{\cdot}5 - {\cdot}695t. \end{aligned}$$

(3) The conditions through which the substance passes in this experiment are practically represented by a *vertical line* in the middle of the liquid and saturated vapour area.

Passage from gaseous to liquid condition without condensation

Andrews, starting with a quantity of carbon dioxide gas at 13° C., represented by A, heated it at constant volume till it reached the 40° C. isothermal at B. It was then compressed at 40° C. until the volume was *less than that occupied by the liquid when just entirely condensed at* 13° C. This was represented by C. It was then cooled at constant volume to D on the 13° C. isothermal.

It was entirely gaseous at A, for, on increasing the pressure, condensation occurred and it was certainly liquid at D, for, on decreasing the pressure, it boiled, but throughout the passage from A to D the substance remained homogeneous.

This is a splendid example of the continuity of state.

The Triple Point for Water

I. Steam Line

We may draw a curve connecting temperature and maximum vapour pressure. The curve is called the "Steam Line." It is also the curve that connects Boiling Point and pressure. The vapour pressure increases with temperature. If you increase the pressure at a given temperature, the vapour will all condense. Thus to the right of the line we have aqueous vapour and to the left of the line water.

II. Ice Line

We may draw a second curve connecting Melting Point and pressure. The curve is called the "Ice Line." The Melting Point of ice is lowered by pressure, though this is exceptional. If you increase the pressure at a given temperature, the ice will all melt. Thus to the right of the line we have water and to the left of the line ice.

III. Hoar Frost Line

We may draw a third curve connecting temperature and the maximum vapour pressure of ice. The curve is called the "Hoar Frost Line." The vapour pressure increases with temperature. If you increase the pressure at a given temperature, the vapour will all *sublime*. Thus to the right of the line we have aqueous vapour and to the left of the line ice.

These three lines meet in a point called the "Triple Point." Thus we get a diagram of the character shown.

It is not difficult to show that the three lines must meet in a point.

Suppose they did not meet in a point, but were arranged as shown in the diagram. Take a point inside ABC. It is below the ice line and is therefore *ice*. It is above the steam line and is therefore *water*. It is below the hoar frost line and is therefore *aqueous vapour*. This is absurd.

Note that for substances which *contract on solidifying* the Melting Point curve goes the other way.

THE KINETIC THEORY OF GASES

The Kinetic Theory of Gases is a theory that has been put forward to explain the physical properties of gases in terms of the motion of their ultimate constituent particles.

Mode of Transformation of Energy into Heat

Experiments upon the "Mechanical Equivalent of Heat" have proved that there is an exact equivalence between heat and energy.

If a moving body is suddenly brought to rest under such conditions that its kinetic energy has no opportunity of passing into potential energy, a quantity of heat will be generated proportional to the kinetic energy possessed by the body at the instant before its motion was arrested.

Suppose a drop of mercury falls from a height on to a plate of glass. The mercury moves *as a whole* through the air, i.e. there is practically no *relative motion* between its parts up to the instant that the glass is struck. Just before striking the glass the mercury has kinetic energy equal to $\frac{1}{2}mv^2$. On reaching the glass the motion of the drop *as a whole* ceases and *relative motions* between the different parts of the mercury take its place. It becomes divided into numerous droplets, which splash off in different directions with various velocities. The sum of the kinetic energies possessed by these various droplets will, however, be equal to the kinetic energy possessed by the main drop at the instant before it struck the glass, i.e. relative motion in the several parts of the body is produced by the arrest of the motion of the body as a whole.

It is probable that, when the motion of a *body* is suddenly arrested, the heat generated is associated with the production of relative motions of the constituent particles in the way suggested above.

Molecular Constitution of a Gas

It is thought that a gas consists of molecules in rapid motion, the progress of a molecule in any direction being limited simply by the occurrence of collisions with other molecules. The average distance between neighbouring molecules is supposed to be *so great* that the effects of their mutual attractions may be left out of account.

Suppose a *perfectly elastic sphere* were set in motion inside an enclosure bounded by *perfectly rigid walls*. Every time the sphere impinged upon one of these walls, the component of its velocity perpendicular to the wall would be *reversed* and a certain force would be exerted on the wall. *No work would be done, however, since the wall is rigid.* The sphere would, therefore, be moving afterwards with the *same velocity as before.* Thus the kinetic energy of the sphere would remain constant.

Let us suppose that a number of perfectly elastic spheres are enclosed by a vessel with rigid walls. The *magnitude* of the velocity of a sphere will not be altered by impact at a wall, but, when two of the spheres meet, their velocities before and after impact will not necessarily be the same. Thus the energy possessed by a particular sphere will vary from time to time. On the other hand, *the total energy possessed by all the spheres will remain constant*, because no energy is communicated to the walls, since they are rigid and the energy lost at any particular impact by one sphere is necessarily gained by another.

Pressure exerted by a Gas

If we consider a gas to consist of elastic spheres in rapid motion, continually colliding with each other or rebounding from the walls of the containing vessel, it is clear that, every time the momentum of a molecule is reversed by impact with a wall of the vessel, a certain force will be exerted on the wall.

Suppose the gas is contained in a cylinder having a frictionless piston. Then the reversal of the momentum, when a molecule strikes the piston, will tend to move the piston outwards, so as to increase the volume occupied by the gas. In other words, *the reversal of the momentum produces a pressure on the piston.* This pressure is the "pressure of the gas."

To deduce Boyle's Law from the Kinetic Theory of Gases

We shall make the following assumptions:—

1. That the diameter of a molecule is very small compared with the distance traversed between successive encounters.

2. That a very large number of molecules exist even in the smallest volume of gas with which we are acquainted.

3. That the molecules are moving with considerable velocities, so that a large number of encounters occur in an exceedingly short interval of time.

4. That the time occupied by an encounter of two molecules is very small in comparison with the interval elapsing between successive encounters.

5. That the molecules are, on an average, so far separated from one another, that the effects of their mutual attractions or repulsions may be neglected.

Let us suppose that a certain quantity of gas is contained in a cubical vessel, each edge of which is 1 cm. long. Then the force produced by the reversal of the momenta of the molecules impinging on one face of the cube will be equal to the pressure exerted by the gas, since

$$\text{pressure} = \text{force per unit area.}$$

Let there be n molecules contained in the vessel.

$$\text{Volume of vessel} = 1 \text{ c.c.}$$

$$\text{Volume of each molecule} = \frac{1}{n} \text{ c.c.}$$

Each molecule may be supposed to *occupy a small cube* having this volume. The molecules will move backwards and forwards in these small cubes, the directions of their motions being reversed by impact on the walls of the containing vessel, or by collisions with other molecules.

If one molecule moves out of the small cube, another will, *on an average*, immediately enter and take its place.

A molecule will move freely in the interval between successive encounters with other molecules. The distance traversed will be equal to the length of the imaginary cube in which the molecule moves backwards and forwards. This distance is called the "mean free path" of the molecule.

Let *abcd* be a face of one of the n imaginary cubes occupied by the gas molecules and let it be in the plane of one of the bounding surfaces of the cubical containing vessel. Then, if the contained molecule moves backwards and forwards *along the normal* to *abcd* with an average velocity of V cms. per sec., it will cover a distance $2d$ between successive impacts on *abcd*, where

$d =$ length of an edge of the small cube or the mean free path of the molecule.

Now

$$\text{volume of small cube} = d^3 = \frac{1}{n}.$$

$$\therefore\ d = \left(\frac{1}{n}\right)^{\frac{1}{3}} = \frac{1}{n^{\frac{1}{3}}}\text{ cm.}$$

$$\text{Number of impacts per sec. on } abcd = \frac{V}{2d} = \frac{V}{\dfrac{2}{n^{\frac{1}{3}}}} = \frac{n^{\frac{1}{3}}V}{2}.$$

If $m =$ mass of a molecule,

$$\text{momentum of molecule just before impact} = mV,$$

$$\text{momentum of molecule just after impact} = -mV.$$

$$\therefore\ \text{Change of momentum at a single impact} = 2mV.$$

This change takes place $\dfrac{n^{\frac{1}{3}}V}{2}$ times per sec.

$\therefore$ Total change of momentum per sec. on surface *abcd*

$$= 2mV \times \frac{n^{\frac{1}{3}}V}{2} = n^{\frac{1}{3}}mV^2.$$

But change of momentum per sec. or rate of change of momentum

$$= \text{force}.$$

$$\therefore \text{ Force exerted on the area } abcd = n^{\frac{1}{3}} m V^2 \text{ dynes.}$$

$$\text{Area of } abcd = d^2$$

$$= \left(\frac{1}{n^{\frac{1}{3}}}\right) \times \left(\frac{1}{n^{\frac{1}{3}}}\right)$$

$$= \frac{1}{n^{\frac{2}{3}}} \text{ sq. cm.}$$

$$\text{Number of squares such as } abcd \text{ in 1 sq. cm.} = \frac{1}{\frac{1}{n^{\frac{2}{3}}}}$$

$$= n^{\frac{2}{3}}.$$

$$\therefore \text{ Force exerted on a face of the cm. cube} = n^{\frac{1}{3}} m V^2 \times n^{\frac{2}{3}}$$

$$= nmV^2 \text{ dynes.}$$

$$\therefore \text{ Pressure of contained gas} = nmV^2 \text{ dynes per sq. cm.}$$

Since a molecule may not always be moving with the same velocity and the velocities of different molecules at the same instant are not exactly equal, V^2 will represent *the mean value of the square of the molecular velocity.*

We have assumed so far that all the molecules are moving either backwards or forwards along a line perpendicular to *abcd*. As a matter of fact, if any three lines are drawn at right angles to each other, e.g. parallel to the adjoining edges of the cm. cube, as many molecules will, at any instant, be moving along one of these lines as along another. Thus, since only *one third* of the total number of molecules should be assumed to be moving in any one direction at any instant, we must write $\frac{n}{3}$ instead of n in the equation just obtained.

$$\therefore \text{ Pressure on one face of the cm. cube} = \frac{nmV^2}{3} \text{ dynes per sq. cm.}$$

$$= p.$$

Multiplying both sides of the equation by v, which may represent *any* volume measured in c.c., we get

$$pv = \frac{nmvV}{3}$$

Now nm = mass of n molecules, originally occupying 1 c.c.

$\therefore$ nm = density of the gas at the initial pressure and a temperature which has been assumed to be constant.

$\therefore$ nmv = mass of gas which occupies, at the temperature in question, a volume v under a pressure of $\frac{nmV^2}{3}$.

Let this mass, $$nmv = M.$$

Then $$pv = \frac{MV^2}{3}.$$

Consequently the relation

$$pv = \text{constant}$$

will hold as long as V^2, the average value of the square of the velocities of the molecules of the gas, remains unaltered.

But, since $\frac{1}{2}mV^2$ is the kinetic energy of a gas molecule due to its linear motion, $\frac{1}{2}MV^2$ will be the kinetic energy possessed by a mass, M, of the gas, in virtue of the linear motions of its constituent molecules.

Hence, since we have assumed that an increase in the kinetic energy of the molecules of a gas is the cause of a rise in its temperature, we see that *the relation*

$$pv = \text{constant}$$

will hold as long as the temperature remains unaltered.

Relation between the temperature of a gas and the linear velocities of its constituent molecules

By the combination of Boyle's and Charles' Laws

$$\frac{p_1v_1}{T_1} = \frac{p_2v_2}{T_2},$$

i.e. $$\frac{pv}{T} = \text{constant}$$

$$= R.$$

$$\therefore\ pv = RT.$$

Now we have just proved that $$pv = \frac{MV^2}{3}.$$

$$\therefore\ RT = \frac{MV^2}{3}.$$

And since R and $\frac{M}{3}$ are constants for a given mass of gas, it is clear that

$$T \propto V^2,$$

i.e. the absolute temperature of a gas is proportional to the mean square of the molecular velocity or to the kinetic energy possessed by the molecules of the gas in virtue of their linear velocities.

If we take a volume, v, of gas and cool it *at constant pressure*, since

$$pv = \frac{MV^2}{3},$$

$$pv = RT,$$

we shall have $v = 0$,

when $V^2 = 0$

and $T = 0$.

Again, if a gas is cooled *at constant volume*,

we shall have $p = 0$,

when $V^2 = 0$

and $T = 0$.

Hence the absolute zero may be defined as follows:—

Def. "The absolute zero is the temperature at which the linear velocities of the molecules have been reduced to zero, i.e. when the molecules have been reduced to rest."

Avogadro's Hypothesis

Avogadro's Hypothesis states that "equal volumes of gases, at the same temperature and pressure, contain equal numbers of molecules."

It follows, from what has gone before, that the temperature of a gas molecule is proportional to the kinetic energy possessed by it in virtue of its linear velocity.

It is generally assumed that, *at a given temperature*, the average kinetic energies possessed by single molecules of *different gases* have equal values.

Let m_1 = mass of a molecule of a gas A,

V_1 = average velocity at absolute temperature $T°$,

m_2 = mass of a molecule of a gas B,

V_2 = average velocity at absolute temperature $T°$.

K.E. = kinetic energy.

Then K.E. of a molecule of A at $T° = \frac{1}{2} m_1 V_1^2$,

K.E. of a molecule of B at $T° = \frac{1}{2} m_2 V_2^2$.

According to the above assumption

$$\tfrac{1}{2} m_1 V_1^2 = \tfrac{1}{2} m_2 V_2^2.$$

$$\therefore\ m_1 V_1^2 = m_2 V_2^2 \quad \text{....................................(1).}$$

Let us suppose that two centimetre cubes are respectively filled with the gases A and B, at the same temperature $T°$ and pressure p.

Then, if $n_1, n_2 =$ number of molecules in the respective cubes,
we have seen previously that

$$p = \frac{n_1 m_1 V_1^2}{3} = \frac{n_2 m_2 V_2^2}{3}.$$

$$\therefore\ n_1 m_1 V_1^2 = n_2 m_2 V_2^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2).$$

Dividing (2) by (1)

$$n_1 = n_2.$$

This proves Avogadro's Hypothesis.

Graham's Law of Diffusion

Graham found that different gases diffused through porous plugs at rates which were inversely proportional to the square roots of their densities.

From (2), in what has gone before, we get

$$\frac{V_1^2}{V_2^2} = \frac{n_2 m_2}{n_1 m_1}.$$

$$\therefore\ \frac{V_1}{V_2} = \sqrt{\frac{n_2 m_2}{n_1 m_1}}$$

$$= \sqrt{\frac{\text{density of } B}{\text{density of } A}},$$

i.e. the average velocities of the molecules of different gases, at the same temperature and pressure, are inversely proportional to the square roots of their densities.

This proves Graham's Law of Diffusion.

Pressure of a mixture of Gases or Vapours

One of Dalton's Laws of Vapour Pressure states that "The pressure exerted by a vapour is independent of the presence of any other vapour or gas, which has no chemical affinity for it." The pressure of a mixture of gases and vapours enclosed in a given space is therefore equal to the *sum* of the pressures which the gases and vapours would *severally* exert, when individually occupying the given space at the same temperature.

This follows from the Kinetic Theory of Gases, as the following argument shows:—

The pressure p exerted by a mixture of two gases, of which the molecules have masses m_1 and m_2, and velocities V_1 and V_2, respectively, is given by the equation

$$p = \frac{n_1 m_1 V_1^2}{3} + \frac{n_2 m_2 V_2^2}{3},$$

n_1 and n_2 being, respectively, the number of molecules of different kinds in 1 c.c. This expression is clearly equal to the sum of the pressures which would be exerted by n_1 molecules of the first gas and n_2 molecules of the second gas, if these were severally enclosed in separate vessels, each of unit volume.

To find the work performed in compressing a gas isothermally

Let A be a piston working in a cylinder B and let the pressure of the enclosed gas be p. Let the piston move inwards through a small distance dx—*small, since, if it is great, the pressure, p, will vary appreciably.*

Let area of piston $= a$.

Then force on piston $= p \times a$,

$$\therefore \text{work done} = \text{force} \times \text{distance} = pa \times dx = padx.$$

But $adx =$ decrease in volume $= dv$,

$$\therefore \text{work done} = pdv.$$

The work done in compressing a gas may be found graphically as follows:—

Let $ABCD$ represent the isothermal for the gas enclosed in the cylinder.

Let $OF =$ initial volume,

$FG = dv$.

Then work done $= pdv$

$= CF \times FG$

$=$ area of rectangle $CFGH$.

This is only true if dv is small.

If the volume is decreased to OE, work done = area of figure $CFEB$.

This is a typical method for finding the work done graphically. It is employed, for instance, in finding the work done in the case of the "Indicator Diagram" of an engine.

The only other method is by the integral calculus.

Indirect method for finding the two Specific Heats of a Gas

Let us consider unit mass of gas contained in a vessel with a movable piston and let us suppose that the temperature is raised through a small range $dT°$.

Heat required to raise unit mass at constant volume

$$= \text{specific heat at constant volume} \times \text{rise in temperature}$$

$$= C_V \times dT.$$

Heat required to raise unit mass at constant pressure

$$= \text{specific heat at constant volume} \times \text{rise in temperature} + \text{heat equivalent of the work done against the atmosphere}$$

$$= C_V \times dT + \frac{pdv}{J},$$

where dv = small increase in volume,

J = Joule's Mechanical Equivalent of Heat.

But heat required to raise unit mass at constant pressure

$$= C_P \times dT.$$

$$\therefore C_P dT = C_V dT + \frac{pdv}{J}.$$

If the gas obeys Boyle's Law, pdv can be calculated as follows:—

$$pv = RT,$$

$$p(v+dv) = R(T+dT),$$

$$pv + pdv = RT + RdT,$$

$$\therefore pdv = RdT.$$

$$\therefore C_P dT = C_V dT + \frac{RdT}{J}.$$

$$\therefore C_P = C_V + \frac{R}{J}.$$

Dividing by C_V,

$$\frac{C_P}{C_V} = 1 + \frac{R}{J \,.\, C_V}.$$

It is found that $\frac{C_P}{C_V}$ is constant for a given gas and it can be determined either by a determination of the velocity of sound in the gas or by the method of Clément and Desormes. It is called by the letter γ.

$$\therefore \gamma = 1 + \frac{R}{J \,.\, C_V}.$$

Here everything but C_V is known and hence this latter can be found.

C_P can be found from the relation

$$\frac{C_P}{C_V} = \gamma.$$

$$\therefore C_P = \gamma \, . \, C_V.$$

It should be noted that there is no need, in what has gone before, to make either the rise in temperature or the increase in volume small, since *at constant pressure* p is constant and in any case

$$\text{work done} = pdv$$

$$\text{or } pv_1,$$

where $v_1 =$ increase in volume.

This was Mayer's Method for finding the Mechanical Equivalent of Heat.

Since $$C_P = C_V + \frac{R}{J},$$

$$\frac{R}{J} = C_P - C_V,$$

$$\therefore J = \frac{R}{C_P - C_V}.$$

(See Elementary Notes.)

To find the value of the constant R for air

Since $$pv = RT,$$

$$R = \frac{pv}{T}.$$

We shall work it out for 1 gm. of air.

Wt. of 1 c.c. of air at 0° C. and 760 mm. = ·001293 gm.

$$\therefore \text{vol. of 1 gm. of air} = \frac{1}{\cdot 001293}$$

$$= 773 \cdot 4 \text{ c.c.}$$

Then $$v = 773 \cdot 4 \text{ c.c.}$$

$$p = 1033 \cdot 6 \text{ gms. wt. per sq. cm.}$$

$$= 1033 \cdot 6 \times 981 \text{ dynes per sq. cm.}$$

$$T = 273^\circ \text{ A.}$$

$$\therefore R = \frac{pv}{T}$$

$$= \frac{1033 \cdot 6 \times 981 \times 773 \cdot 4}{273}$$

$$= \cdot 2872 \times 10^7.$$

This is identical with the expression obtained in Mayer's Method in Elementary Notes except that for 773·4 we had $\frac{1}{\cdot 001293}$.

Two other points should be noticed:—

1. We should get a different value for R, if we took a mass of air other than 1 gm.

2. We should get a different value for R, if we took another gas, such as Hydrogen. In this case

$$\begin{aligned} v &= \frac{1}{\cdot 0000898} \\ &= 11136 \text{ c.c.} \\ R &= \frac{1033\cdot 6 \times 981 \times 11136}{273} \\ &= 4\cdot 14 \times 10^7. \end{aligned}$$

Note that R is a *constant for all gases*, if it is taken for the *molecular weight in gms. of any gas*, since the *volume* of the molecular weight in gms. for any gas is 22·32 litres.

To show how the Ratio of the two Specific Heats of a gas varies with the number of atoms in the molecule

Let V^2 = mean square of the molecular velocity of a gas at a particular temperature $T°$ A.

M = mass of all the molecules.

K.E. = kinetic energy.

Then K.E. of the gas $= \frac{1}{2} M V^2$.

Let mass of gas = 1 gm.

Then

$$\begin{aligned} \text{K.E.} &= \tfrac{1}{2} V^2 \\ &= \frac{V^2}{2}. \\ \therefore 2\,\text{K.E.} &= V^2. \end{aligned}$$

Again

$$\begin{aligned} pv &= RT = \tfrac{1}{3} M V^2. \\ \therefore RT &= \frac{V^2}{3}. \\ \therefore 3RT &= V^2. \\ \therefore 2\,\text{K.E.} &= 3RT. \\ \therefore \text{K.E.} &= \tfrac{3}{2} RT. \end{aligned}$$

Let us suppose that the temperature rises by 1 C.° Then the K.E. changes from $\frac{3}{2} RT$ to $\frac{3}{2} R(T+1)$,

$$\text{i.e. gain in K.E. per C.}^\circ = \tfrac{3}{2}R(T+1) - \tfrac{3}{2}RT$$
$$= \tfrac{3}{2}R.$$

This is the increase per C.° in the energy due to the linear velocities of the molecules in 1 gm. of the gas.

If we assume that a gas consists of a large number of rapidly moving molecules, a rise in temperature may have three effects:—

1. The velocity with which the molecules move from point to point may increase.

2. The velocity with which the component parts of the molecules, i.e. the atoms, move within the molecule may increase.

3. The velocity with which the different parts of the atom move within the atom itself may increase.

This last possibility may be neglected, as being too small to affect the result.

Then, if E_M = gain in energy of the molecules per C.°,

E_A = gain in energy of the atoms per C.°,

$$\gamma = \frac{C_P}{C_V}$$
$$= \frac{E_M + E_A + pdv}{E_M + E_A}.$$

Now we have seen that

$$E_M = \tfrac{3}{2}R,$$
$$pdv = Rdt.$$

$\therefore$ when $dt = 1$,

$$pdv = R.$$
$$\therefore \gamma = \frac{E_M + E_A + pdv}{E_M + E_A}$$
$$= \frac{\frac{3}{2}R + E_A + R}{\frac{3}{2}R + E_A}$$
$$= \frac{3R + 2E_A + 2R}{3R + 2E_A}$$
$$= \frac{5R + 2E_A}{3R + 2E_A}.$$

Now, for a monatomic gas,

$$E_A = 0.$$
$$\therefore \gamma = \frac{5R}{3R}$$
$$= 1{\cdot}66.$$

This value for γ is confirmed by experiment; e.g. mercury vapour, which is monatomic, gives 1·66.

Moreover, from the value of γ for any gas, a rough estimate of the number of atoms in the molecule can be arrived at, as the following argument shows:—

$$\gamma = \frac{3R + 2E_A + 2R}{3R + 2E_A}$$

$$= 1 + \frac{2R}{3R + 2E_A}.$$

Now, for monatomic molecules,

$$E_A = \text{zero},$$

therefore γ for monatomic molecules is a maximum, 1·66.

As the number of atoms in the molecule increases, E_A becomes greater and therefore the expression

$$\frac{2R}{3R + 2E_A}$$

becomes less and γ becomes less, as is shown by the following table:—

Gas	No. of atoms	γ
Argon	1	1·66
Hydrogen	2	1·42
Oxygen	2	1·40
Chlorine	2	1·30
Bromine	2	1·29
Carbon dioxide	3	1·26
Marsh gas	5	1·26
Ethene	6	1·12
Ethyl alcohol	9	1·11
Ether	15	1·05
Turpentine...	26	1·03

The fact that, in the case of argon, helium, krypton, neon and xenon, the value of γ, obtained by the velocity of sound method, was found to be 1·66, has been taken as evidence that these gases are *monatomic*. This was very important in determining the *atomic weights* of these elements.

ADIABATICS

Heat is generated when a gas is compressed. If this takes place in a vessel through which the heat can be transmitted, you get an "isothermal change," whereas, if the vessel is one through which heat cannot be transmitted, you get an "adiabatic change" (*α-δια-βαινω*).

We may represent the relation between the pressure and volume of a gas in this case by an "adiabatic curve."

Let A represent the condition of a gas. If the *volume* is decreased from OG to OF *isothermally*, the pressure will become FB, B being situated on the isothermal CBA. If the *volume* is decreased *adiabatically*, the pressure will be *greater* than FB, owing to the heat produced in the compression. Let it become FD. Then D is a point on the adiabatic curve passing through A. Note that it is *steeper* than the isothermal curve.

The relation between pressure and volume instead of being

$$PV = \text{constant},$$

is

$$PV^\gamma = \text{constant},$$

where

$$\gamma = \text{ratio of the two specific heats.}$$

It should be noticed that, if the volume at A is *increased adiabatically*, the pressure will be less than it would be isothermally owing to the heat *absorbed* in the expansion.

The adiabatic curve can be drawn by taking a point on the isothermal curve and calculating what the pressure would become for any volume.

Let

$P_1 = $ 1st pressure,
$V_1 = $ 1st volume,
$P_2 = $ 2nd pressure,
$V_2 = $ 2nd volume.

Then

$$P_2V_2^\gamma = P_1V_1^\gamma,$$

$$\therefore\ P_2 = P_1\frac{V_1^\gamma}{V_2^\gamma}$$

$$= P_1\left(\frac{V_1}{V_2}\right)^\gamma.$$

Using this formula we obtained the following numbers:—

V	Isothermal P	Adiabatic P
5	80	187·7
10	40	70·7
20	20	26·6
40	10	10
60	6·66	5·6
80	5	3·8

To prove that the Isothermal Elasticity of a gas is equal to P and that the Adiabatic Elasticity of a gas is equal to Pγ.

Let the initial pressure, P, be increased by p. Then the volume, V, will be decreased by v.

1. Isothermally.

$$P_1 V_1 = P_2 V_2,$$
$$PV = (P+p)(V-v).$$
$$\therefore PV = PV - pv + pV - Pv.$$

Now pv is negligible, since p and v are very small.

$$\therefore Pv = pV,$$
$$\therefore P = \frac{pV}{v}$$
$$= \frac{\frac{pV}{V}}{\frac{v}{V}}$$
$$= \frac{p}{\frac{v}{V}}$$
$$= E.$$

Isothermal Elasticity $= P$.

2. Adiabatically.

$$P_1 V_1^\gamma = P_2 V_2^\gamma,$$
$$PV^\gamma = (P+p)(V-v)^\gamma.$$

Dividing both sides by V^γ,

$$P = (P+p)\left(1-\frac{v}{V}\right)^\gamma,$$
$$\left[\frac{(V-v)^\gamma}{V^\gamma} = \left(\frac{V-v}{V}\right)^\gamma\right.$$
$$\left. = \left(1-\frac{v}{V}\right)^\gamma\right].$$

Now $$\left(1-\frac{v}{V}\right)^\gamma = 1-\gamma\frac{v}{V},$$
$$[(1-x)^2 = 1-2x+x^2$$
$$(1-x)^3 = 1-3x+3x^2-x^3.$$
$$(1-x)^{10} = 1-10x+\text{etc.}$$
$$(1-x)^\gamma = 1-\gamma x+\text{etc.}$$

Since, x being very small, x^2 etc. may be neglected,

$$\therefore (1-x)^\gamma = 1 - \gamma x.]$$

$$\therefore P = (P+p)\left(1 - \gamma \frac{v}{V}\right).$$

$$\therefore P = P - \gamma \frac{pv}{V} + p - \gamma \frac{Pv}{V}.$$

Neglecting $\gamma \frac{pv}{V}$,

$$\gamma \frac{Pv}{V} = p.$$

$$\therefore P\gamma = \frac{p}{\frac{v}{V}}$$

$$= E.$$

$$\text{Adiabatic Elasticity} = P\gamma.$$

Experimental Determination of γ

1. By finding the specific heat of a gas at constant pressure by Regnault's method and the specific heat at constant volume by Joly's Differential Steam Calorimeter.

Then $$\gamma = \frac{\text{specific heat at constant pressure}}{\text{specific heat at constant volume}}.$$

2. By finding the velocity of sound in a gas.

$$v = \sqrt{\frac{E}{D}}$$

$$= \sqrt{\frac{P\gamma}{D}}.$$

(See "Lecture Notes on Sound.")

Find v by Kundt's tube,
P by determining the pressure,
D by knowing the density of the gas.

Hence calculate γ.

3. Clément and Desormes' Method.

The apparatus consists of a carboy, C, with valve, V, manometer, M, and a tube, T, with a tap, through which air could be pumped. The best liquid to use in the manometer is Fleuss pump oil, which gives off no vapour and has a low specific gravity, so that small variations in pressure can be obtained. In order to thoroughly dry the enclosed gas some strong sulphuric acid is poured into C.

The experiment is performed as follows:—

(1) The valve, V, is closed and air is pumped into C till a pressure equivalent to about 30 cms. of water is indicated by the manometer. The tap is then closed. For some minutes after pumping has been discontinued *the pressure slowly falls.* This is due to the fact that the air, which was heated during its compression, is slowly attaining the temperature of the atmosphere. When the manometer ceases to move, the pressure, P_1, is taken.

(2) The valve, V, is then opened for 1 or 2 secs. and then closed. The enclosed air expands until the pressure is equal to the atmospheric pressure, P. Since the vessel, C, is *large*, comparatively little heat will be communicated to the enclosed air during the expansion, i.e. the air will expand *adiabatically.*

(3) At the instant when V is closed the surface of the oil in the two limbs of the manometer will be level. After a short interval it will be noticed that the manometer indicates *an increasing pressure.* This is due to the fact that the enclosed air, which has cooled by expansion, is now attaining the temperature of the surrounding air. When the manometer ceases to move, the pressure, P_2, is taken.

During the time that the valve, V, was open, a certain quantity of air escaped into the atmosphere. *We will confine ourselves to a portion of air that has remained inside C throughout the experiment.*

Let V_1 = initial volume of *this* air,

P_1 = initial pressure.

Then the initial condition of the air may be represented by the point A on the isothermal EAC corresponding to the temperature of the surrounding air.

When the valve was opened, the air expanded along the adiabatic DAB from A to B, till its pressure was equal to P, the atmospheric pressure. At the instant that the valve was closed the condition of the air corresponded to B.

The valve being closed, the volume of the contained air *cannot alter appreciably,* since the volume of air enclosed by the manometer is small. Hence, as the enclosed air attained the temperature of the atmosphere, its pressure rose from B to C. The point C therefore corresponds to the final state of the air.

Let V_2 = final volume of the air,

P_2 = final pressure,

E_1 = adiabatic elasticity,

E_2 = isothermal elasticity,

p_1 = adiabatic *alteration* in pressure,

p_2 = isothermal *alteration* in pressure.

Then, adiabatically,

$$E_1 = P\gamma = \frac{p_1}{\frac{v}{V_1}},$$

isothermally,

$$E_2 = P = \frac{p_2}{\frac{v}{V_1}}.$$

From the diagram we see that the change in volume v is the same in the two cases.

Dividing,

$$\gamma = \frac{p_1}{p_2}$$

$$= \frac{P_1 - P}{P_1 - P_2}.$$

But we know P_1, P and P_2. Hence γ can be found.

This applies only when p_1, p_2 and v are small, i.e. when P_1, P_2 and P are of *very nearly the same magnitude.*

This may also be worked out in the following manner:—

Since A and C are on an isothermal,

$$P_1 V_1 = P_2 V_2.$$

$$\therefore \frac{V_2}{V_1} = \frac{P_1}{P_2} \quad \text{..(1).}$$

Since A and B are on an adiabatic,

$$P_1 V_1^{\gamma} = P V_2^{\gamma}.$$

$$\therefore \left(\frac{V_2}{V_1}\right)^{\gamma} = \frac{P_1}{P} \quad \text{..(2).}$$

Substituting in (2) the value of $\frac{V_2}{V_1}$ obtained from (1), we get

$$\left(\frac{P_1}{P_2}\right)^{\gamma} = \frac{P_1}{P}.$$

Taking logarithms of both sides of this equation we get

$$\gamma (\log P_1 - \log P_2) = \log P_1 - \log P.$$

$$\therefore \gamma = \frac{\log P_1 - \log P}{\log P_1 - \log P_2}.$$

When P_1, P_2 and P are of *very nearly the same magnitude*,

$$\gamma = \frac{P_1 - P}{P_1 - P_2},$$

which is the formula we obtained before.

We obtained the following results with R. W. Berridge's apparatus:—

$$\begin{aligned} P &= 76{\cdot}52 \text{ cms. of mercury} \\ &= 76{\cdot}52 \times 13{\cdot}6 \text{ cms. of water} \\ &= 1040{\cdot}6 \text{ cms. of water.} \\ p_1 &= 39{\cdot}10 \text{ cms. of oil} \\ &= 39{\cdot}10 \times {\cdot}918 \text{ cms. of water} \\ &= 35{\cdot}9 \text{ cms. of water.} \\ P_1 &= P + p_1 \\ &= 1040{\cdot}6 + 35{\cdot}9 \\ &= 1076{\cdot}5 \text{ cms. of water.} \\ p_2 &= 27{\cdot}32 \text{ cms. of oil} \\ &= 27{\cdot}32 \times {\cdot}918 \text{ cms. of water} \\ &= 25{\cdot}1 \text{ cms. of water.} \\ P_2 &= P_1 - p_2 \\ &= 1076{\cdot}5 - 25{\cdot}1 \\ &= 1051{\cdot}4 \text{ cms. of water.} \end{aligned}$$

Then

$$\begin{aligned} \gamma &= \frac{P_1 - P}{P_1 - P_2} \\ &= \frac{1076{\cdot}5 - 1040{\cdot}6}{1076{\cdot}5 - 1051{\cdot}4} \\ &= \frac{35{\cdot}9}{25{\cdot}1} \\ &= 1{\cdot}431, \end{aligned}$$

or

$$\begin{aligned} \gamma &= \frac{\log 1076{\cdot}5 - \log 1040{\cdot}6}{\log 1076{\cdot}5 - \log 1051{\cdot}4} \\ &= \frac{3{\cdot}0320 - 3{\cdot}0173}{3{\cdot}0320 - 3{\cdot}0216} \\ &= \frac{147}{104} \\ &= 1{\cdot}414. \end{aligned}$$

Value for γ.

By experiment = 1·414.
By book = 1·405.

THE STEAM ENGINE

The essential parts of a steam engine are as follows:—

1. The Boiler.

By the heat of combustion of the fuel the boiler and its contents are kept at a nearly constant temperature above 100° C. and consequently the space above the water is always occupied by steam at a constant pressure, greater than that of the atmosphere.

2. The Cylinder.

This is fitted with a piston, attached to a rod, which passes steam-tight through one end of the cylinder.

3. The Condenser.

This is a vessel kept free of air by a pump worked by the engine and maintained at a low temperature by a jet of cold water, or by being surrounded with cold water. The pressure is therefore much less than that of the atmosphere.

To set the engine at work, communication is made between the boiler and one end of the cylinder, and between the condenser and the other end. The two surfaces of the piston are thus exposed to pressures which depend upon the temperature of the boiler and condenser respectively, and the piston is urged towards one end of the cylinder with a force corresponding to the difference of these pressures. When the piston gets to the end of its stroke, the communications between the boiler and condenser, respectively, and the cylinder are inverted by means of a "slide valve," and the piston is therefore urged with the same force as before towards the opposite end. Then a second inversion of the communications causes the piston to be driven in the same direction as at first, and this is repeated over and over again.

Summary of the processes which go on in a steam engine

1. Communication of heat to the "working substance" from a hotter body, the "source" or boiler.

2. Transformation of *some* of this heat into work by the expansion of the working substance in the cylinder.

3. Communication of the heat not transformed to a colder body, the condenser.

Relation between Heat and Work in a Steam Engine

Hirn found that *less* heat was conveyed to the condenser than was carried from the boiler, and the number he obtained for the ratio of the work done to the heat which disappears was very nearly the same as that obtained by Joule as the result of his experiments on friction.

Hirn obtained the following results:—

1. The quantity of heat, Q_1, carried from the boiler to the cylinder, always exceeds the quantity, Q_2, carried from the cylinder to the condenser.

2. The difference, $Q_1 - Q_2$, is proportional to the external work done by the engine, i.e., if $W =$ work done,

$$\frac{W}{Q_1 - Q_2} = \text{constant}, \qquad = J,$$

where $J =$ Joule's Mechanical Equivalent of Heat.

Conditions necessary for the production of work by the expenditure of heat

1. It is necessary that we should have two bodies at different temperatures. The continuous performance of work by a heat engine is always attended by the transfer of heat from a hotter to a colder body.

2. When heat passes by conduction or radiation between two bodies *no external work is done.* Something else is therefore necessary in addition to the two bodies at different temperatures. *This is an intermediate body capable of changing its volume on the application of heat.* It must be placed, first, in contact with the hot body, so that it takes in heat, and then carried to the cold body, to which it gives out heat. By the changes of volume produced by taking in and giving out heat, work may be done. The hot body is the boiler, the cold body the condenser and the intermediate body the water changed into steam.

3. Heat is wasted, as far as the production of work is concerned, when it passes between bodies at different temperatures *by conduction.* The engine will therefore be *most effective,* when the intermediate body is at the same temperature as the hot body while it takes in heat and at the same temperature as the cold body while it gives out heat.

INDICATOR DIAGRAMS

If we draw two straight lines, OA, OB, at right angles to one another and agree that distances measured from O along OA shall represent pressures and distances measured along OB shall represent volumes, then any point, C, may be regarded as representing the condition of a substance, as far as its volume and pressure are concerned.

If the volume and pressure of the substance undergo any alteration, but are always represented by the point C, it is clear that C must change its position and, since the condition of the substance cannot change *except by a steady increase or decrease*, it follows that the point C must move along some definite line, which is generally curved. This line will represent graphically the law connecting the variations in volume and pressure, which the substance undergoes. Such a line is called an "Indicator Diagram."

Watt's Indicator

The indicator diagram was first employed by James Watt to indicate the pressure and volume of steam in the cylinder of an engine, on one side of the piston, at every point throughout the stroke.

In Watt's indicator the pressure was indicated by a pencil, which was attached to a piston moving in a *very small cylinder*, to which the steam from the engine cylinder had access. The piston was pressed down by a spring, while the steam, gaining access to its lower side, forced it up against the pressure of the spring. Now the compression or extension of a spring is *proportional to the force applied.* Hence the pencil was raised through a distance proportional to the *excess* of the pressure of steam in the cylinder over the atmospheric pressure. If the pressure of the steam were *less* than atmospheric, the pencil was depressed through a corresponding distance.

As the pencil moved, it traced a line upon a sheet of paper attached to a board, which could be made to move in exactly the same way as the piston *of the engine*, though the length of the traverse was reduced.

If the pressure in the cylinder remained constant, a horizontal line would be traced by the pencil. If the pressure increased or diminished, when the board was stationary, or changed *suddenly*, when the board was moving, a vertical line would be the result. A steady change of pressure accompanying the change of position of the piston would cause a curved line to be described.

It was found, however, that, although the traverse of the pencil was only a few inches, when the pressure varied rapidly, the *kinetic energy* acquired by the *little* piston was sufficient to carry it and the pencil far beyond the position corresponding to the steam pressure. This difficulty was got over by allowing the piston to move only through a *very small distance*, correspondingly strong springs being used, and the motion of the piston *multiplied* in the pencil by a system of levers.

In all indicators now in use the paper is wrapped upon a *cylinder on a drum*, which is made to revolve through rather less than one revolution by the motion of the piston of the engine and is made to return by a spring contained within the instrument.

Normal Indicator Diagrams

If the steam from the boiler be allowed full access to the cylinder during the whole of the forward stroke of the piston and the steam in the cylinder be allowed to escape freely into the air during the whole of the backward stroke, the ports being opened and closed at the instant when the piston is at the extreme end of its stroke, the diagram traced by the indicator will be a *rectangle*, the upper side, AB, corresponding to *boiler pressure* and the lower side, CD, to *atmospheric pressure.* The diagrams of some *steam fire engines* are of this character, for, in these engines, the object is to get as much work as possible from the engine in a given time *regardless of the expenditure of fuel.* Hence the full boiler pressure of the steam is sustained till the end of the stroke.

But in all engines in the working of which *economy* is a consideration, the "exhaust steam" is not allowed to escape at full boiler pressure but, the supply from the boiler being cut off *long* before the stroke is completed, the steam in the cylinder is made to expand, doing work as it expands, and is not allowed to escape until its pressure has been reduced very much below that of the steam in the boiler. The diagram is typical of a high-pressure engine working "expansively." The line, AB, represents the condition of affairs during the period of admission and, the communication being open with the boiler, the pressure is maintained nearly equal to that in the boiler itself. At B the steam port is closed and the steam, being confined within the cylinder, *expands* as the piston continues its motion, tracing out the curve BC, until, at the point C, the exhaust port is opened and, the steam being allowed to escape, the pressure falls rapidly almost to atmospheric pressure. At D the piston is at the extremity of its stroke; it then returns, the indicator tracing out the line DE with the exhaust port open until, on the piston arriving at E, the exhaust port is closed and the small amount of steam remaining in the cylinder is compressed so as to form an elastic cushion and assist the rebound of the piston. The compression portion of the curve is represented by EF, and at F the steam port is opened and the pressure rises immediately to full boiler pressure.

Detection of defects in an engine by the indicator diagram

The indicator diagram of an engine generally shows whether the engine is working properly or whether there is anything wrong with the pistons, valves, steam-ways, etc.

1. A leaky piston would be betrayed by the expansion curve *falling much more rapidly* than is consistent with the law of expansion of steam under the conditions existing in the cylinder.

2. If the steam-pipe from the boiler is too small, or if the steam port is not opened wide enough and quickly enough, when the piston commences its stroke, the supply of steam will not keep pace with the piston and the line corresponding to the period of admission *will slope downwards* from A to B. The limiting of the steam supply is called "wire-drawing" and the steam is said to be "wire-drawn."

3. If the exhaust port does not allow a sufficiently ready exit for the steam, the line DE, instead of practically coinciding with the atmospheric line, will be *considerably above it.* This shows that some of the work done by the steam in expanding is employed in overcoming *the back pressure on the other side of the piston,* which detracts from the work done by the engine.

Abnormal Indicator Diagrams

The diagram is a copy of one taken from an engine employed in blowing a fan. It will be noticed that the compression commences at E, or at about one half stroke, and the piston in its motion from right to left compresses the steam in the cylinder, until, when the steam port is opened at F, the pressure is considerably greater than that of the steam in the boiler and the first effect of the opening of the steam port is the fall of the pressure in the cylinder down to that existing in the boiler. As the piston advances, the supply of steam is insufficient to keep up the pressure in the cylinder and the consequent "wire-drawing" is indicated by the downward slope of the admission line, AB. Such a diagram shows that there is a great waste of energy accompanying the working of the engine.

A readjustment of the slide valve, making the compression much later and the opening of the steam ports earlier, so that there may be a wider aperture for the admission of the steam when the piston advances, would enable the engine to do the same amount of work with a much smaller supply of steam and, consequently, a smaller consumption of fuel.

Calculation of the Work Done

If the pressure on the piston remained constant, the work done during a single stroke of the engine would be equal to the resultant force upon the piston multiplied by the length of the stroke. In estimating the resultant force we must take into account the pressure on *both* sides of the piston.

Let area of piston = 80 sq. ins.,
pressure on one side = 60 lbs. wt. per sq. in.,
pressure on other side = 17 lbs. wt. per sq. in.,
length of stroke = 2 ft.
Then resultant pressure = 60 − 17
= 43 lbs. wt. per sq. in.,
resultant force = 43 × 80
= 3440 lbs. wt.
Work done during a single stroke = 3440 × 2
= 6880 ft. lbs.

If similar conditions obtain during the return stroke, the whole of the work done for one revolution of the engine
= 6880 × 2
= 13,760 ft. lbs.

But, instead of considering the pressure on both sides of the piston *at once,* it is generally more convenient to *credit* the steam on one side of the piston with the whole of the work it does during the advance and *debit* it with the work which has to be done against the steam pressure *on the same side* during the return of the piston. *The balance* is the amount of *useful work* obtained from the steam on *that* side of the piston during the complete revolution of the engine. The steam on the other side is then treated in the same way.

This is a more convenient method, since the total amount of work done *by* the steam on one side of the piston is shown by the indicator diagram for that side.

There are two cases to consider:—

1. Let us suppose that, during the whole of the forward stroke of the piston, the pressure is *constant*, and *constant*, but considerably less, during the return stroke.

Then, in the diagram,

if AB = line representing the pressure during the forward stroke,

DC = line representing the pressure during the return stroke,

ON = line representing *zero* pressure,

area $ABNO$ = work done *by* the steam on one side of the piston during the *forward* stroke,

area $CNOD$ = work done *against* the pressure of the steam in the cylinder during the *return* stroke,

area $ABCD$ = *useful* work done *by* the steam on one side of the piston during a complete revolution of the engine.

But the area $ABCD$ *is* the indicator diagram *for one end* of the cylinder during the stroke.

If we add to this the area of the diagram for the *other* side of the piston, we obtain the *whole amount* of work done during the double stroke.

2. Let us suppose that the pressure is *variable.*

Then the work done *by* the steam while the piston moves over a very small portion of its stroke *throughout which the pressure may be regarded as constant*, will be equal to the area of a narrow rectangle, such as *efgh*.

Arguing on these lines we obtain the following results:—

Area $ABCNO$ = work done *by* the steam on one side of the piston during the *forward* stroke,

area $CNOD$ = work done *against* the pressure of the steam in the cylinder during the *return* stroke,

area $ABCD$ = *useful* work done *by* the steam on one side of the piston during a complete revolution of the engine.

Note that in the "Abnormal Indicator Diagram" the area of the little loop at the top must be *subtracted* from that of the rest of the diagram in order to show the work done.

To find the Horse Power of an Engine

This can be found from the indicator diagram, but we also require to know

1. Area of piston,
2. Length of stroke,
3. Number of revolutions per min.

Instead of the two latter we may substitute the mean velocity of the piston in ft. per min.

Example

Let diameter of piston of single cylinder engine

$= 14$ ins.,

length of stroke $= 30$ ins.,

number of revolutions per min. $= 50$.

Heights of ten equidistant ordinates correspond, respectively, to $46\frac{1}{2}$, 50, 50, $36\frac{1}{2}$, 25, 18, 13, 9, 6, 4 lbs. wt. per sq. in.

$$\text{Sum of these ten differences of pressure} = 258 \text{ lbs. wt. per sq. in.}$$

$$\therefore \text{ Mean pressure} = \frac{258}{10}$$

$$= 25{\cdot}8 \text{ lbs. wt. per sq. in.}$$

$$\text{Area of piston} = \pi r^2$$

$$= 3{\cdot}14 \times 7^2$$

$$= 3{\cdot}14 \times 49$$

$$= 154 \text{ sq. ins. about.}$$

$$\therefore \text{ Mean force} = \text{pressure} \times \text{area}$$

$$= 25{\cdot}8 \times 154$$

$$= 3973 \text{ lbs. wt. about.}$$

$$\text{Distance travelled by piston per min.} = 30 \times 2 \times 50 \text{ ins.}$$

$$= \frac{30 \times 2 \times 50}{12} \text{ ft.}$$

$$= 250 \text{ ft.}$$

$$\text{Work done per min.} = \text{force} \times \text{distance}$$

$$= 3973 \times 250$$

$$= 993{,}250 \text{ ft. lbs.}$$

$$\text{Horse Power} = \frac{993{,}250}{33{,}000}$$

$$= 30{\cdot}1.$$

$$\text{Horse Power} = 30{\cdot}1.$$

SECOND LAW OF THERMODYNAMICS

Carnot's Heat Engine

Definition of terms

1. Heat engine.

A heat engine is any mechanical contrivance by means of which heat is converted into work.

Steam engines, gas engines, oil engines, hot-air engines are all forms of heat engines.

All heat engines exhibit the characteristic that heat disappears during the performance of work. For instance, during a given time the heat entering the cylinder of a steam engine is greater than that carried away *by the waste steam*, the excess being proportional to the work performed by the engine.

2. Cycle of operations.

In every form of heat engine the transformation of heat into work is effected by subjecting some suitable substance to a cycle of operations (expansion, compression, condensation, etc.), so arranged that the work done *by* the substance during the cycle is greater than the work done *on* it, and useful external work is done at the expense of the heat supplied to the substance.

3. Working substance.

The substance operated on in this way is called the working substance of the engine.

For instance, in steam engines the working substance is steam.

4. Reversible operation.

A reversible operation is one in which the heat effects involved in the *direct* operation are reversed when the operation is *reversed*.

For instance, the isothermal compression of a gas from the state $P_1 V_1 T$ to the state $P_2 V_2 T$ is a *reversible* one, for the work done *on* the gas during compression from volume V_1 to volume V_2 is equal to the work done *by* the gas during expansion from volume V_2 to volume V_1, and the heat *evolved* during compression is equal to the heat *absorbed* during expansion.

On the other hand, the isothermal compression of a steel spring, say, is *not* a reversible operation, since the heat *evolved* during compression, as the result of molecular friction in the steel, is *not* reversed during expansion. The friction in the steel causes heat to be *evolved* during expansion as well.

5. Simple form of heat engine.

Heat engines differ very considerably from one another in the details of their construction. It is therefore advisable in studying the purely thermal side of the subject to select some simple form of engine, so that the attention may be concentrated on the essential features of the thermal operations.

Carnot's Reversible Cycle

Suppose we are provided with a cylinder, *A*, furnished with an air-tight and frictionless piston, and fitted with a quantity of a perfect gas. The piston and sides of the cylinder are impermeable to heat, but the bottom of the cylinder is a perfect conductor. The temperature of the conducting stands, *C* and *D*, are supposed not to change when heat is taken from or added to them. The temperature T_1 is greater than the temperature T_2.

Let us suppose that the gas in *A* is initially at the temperature T_1 and occupies a volume *Oa* under a pressure equal to *aA*. Then the initial condition of the gas is represented by the point *A*.

The following operations may then be performed:—

1. Place the cylinder on the non-conducting stand *B* and allow the gas to expand *adiabatically* till its temperature falls to $T_2°$.

The *adiabatic AB* will be traversed from *A* to *B*, and, during the expansion, a certain amount of external work, equal to the area *ABba*, will be performed *by the gas on external bodies.*

2. Place the cylinder on the conducting stand *D*, which is maintained at a temperature $T_2°$, and force the piston in till the volume of the contained gas has been reduced from *Ob* to *Oc*. It is supposed that the gas remains at the uniform temperature $T_2°$.

Hence, in passing from *B* to *C*, the *isothermal BC* will be traversed.

A certain amount of work, equal to the area *BCcb*, has been performed *by external agency on the gas.* This work has been converted into heat, which has been communicated to the stand *D*. Let the quantity of heat given up to *D* be Q_2.

3. Place the cylinder on the non-conducting stand *B* and force the piston inwards, thus compressing the gas *adiabatically* until its temperature rises to $T_1°$.

The *adiabatic CD* will be traversed from *C* to *D*, and an amount of work, equal to the area *CDdc*, will be performed *by external agency on the gas.*

4. Place the cylinder on the conducting stand *C*, which is maintained at a temperature $T_1°$, and allow the gas to expand until it attains its original volume.

The *isothermal DA* will be traversed from *D* to *A* and an amount of external work, equal to the area *DAad*, will be *performed by the gas on external bodies.* In order that the temperature of the gas may be maintained at $T_1°$, a quantity of heat equivalent to the total work performed must have been communicated to it from the stand *C*. Let the quantity of heat communicated to the gas be Q_1.

In the diagram the area *ABCD* represents the *net* amount of external work performed *by the gas on external bodies.*

The results of the cycle may be summarised as follows:—

(1) The gas, which was initially in the condition represented by *A*, is finally brought back to the same condition.

(2) A quantity, Q_1, of heat was absorbed by the gas whilst at the temperature $T_1°$.

(3) A quantity, Q_2, of heat was given up by the gas whilst at the temperature $T_2°$.

(4) A net amount of external work, equal to the area $ABCD$, has been performed *by the gas on external bodies.*

From the First Law of Thermodynamics the amount of work performed *by the gas on external bodies* during the cycle must be equal to the heat which has disappeared.

$$\text{Work performed} = \text{area } ABCD.$$

$$\text{Heat that has disappeared} = (Q_1 - Q_2).$$

$$\therefore \text{ Area } ABCD = (Q_1 - Q_2).$$

To show that the cycle is reversible

The following operations may be performed:—

1. Starting at A, compress the gas *isothermally* till its volume is diminished to Od. The isothermal AD is traversed and a quantity of work, equal to the area $ADda$, is performed *by external agency on the gas.* A quantity of heat, Q_1, is given out by the gas.

2. Allow the gas to expand *adiabatically* till its temperature falls to $T_2°$. A quantity of work, equal to the area $DCcd$, is performed *by the gas on external bodies.*

3. Allow the gas to expand *isothermally* from C to B. A quantity of work, equal to the area $CBbc$, is performed *by the gas on external bodies.* A quantity of heat, Q_2, is absorbed.

4. Compress the gas *adiabatically* from B to A. An amount of work, equal to the area $BAab$, is performed *by external agency on the gas.*

In the diagram the area $ABCD$ represents the *net* amount of work performed *by external agency on the gas.*

The results of the cycle may be summarised as follows:—

(1) The gas, which was initially in the condition represented by A, is finally brought back to the same condition.

(2) A quantity, Q_1, of heat was given up by the gas whilst at the temperature $T_1°$.

(3) A quantity, Q_2, of heat was absorbed by the gas whilst at the temperature $T_2°$.

(4) A net amount of work, equal to the area $ABCD$, has been performed *by external agency on the gas.*

From the First Law of Thermodynamics the amount of heat which has made its appearance must be equal to the work performed *by external agency on the gas.*

$$\text{Heat that has made its appearance} = (Q_1 - Q_2).$$

$$\text{Work performed} = \text{area } ABCD.$$

$$\therefore (Q_1 - Q_2) = \text{area } ABCD.$$

In the first case, *where external work was performed by the gas on external bodies,* heat was absorbed at a temperature $T_1°$ and part of it was given up at a *lower* temperature $T_2°$. Hence, in this case, *heat flows from a hot body to one at a lower temperature.* In the second case, *where work was performed by external agency on the gas,* heat was absorbed at a temperature $T_2°$ and given out at a *higher* temperature $T_1°$.

Statement of the Second Law of Thermodynamics

1st Def.

"It is impossible for a self-acting machine, unaided by any external agency, to convey heat from a body at a low temperature to one at a high temperature, or heat cannot of itself pass from a cold to a warmer body."

2nd Def.

"It is contrary to all experience that external useful work can be done at the expense of heat derived from the colder of two bodies, or that heat can pass from a cold body to a hot body without the expenditure of work."

3rd Def.

"It is impossible by means of inanimate material energy to derive mechanical effect from any portion of matter by cooling it below the temperature of the surrounding objects." (Lord Kelvin.)

Being a negative statement, the law is hardly founded upon direct experiment. It rather represents the universal experience with regard to heat engines and the general phenomena attending the transference of heat.

It really amounts to this :—" When we seek to transform heat into work, we usually derive the heat from a hotter body, we transform *some* of it and are obliged to give *some* to a colder body, actually heating that colder body."

It must be clearly understood that this only applies to *cyclical operations*, i.e. when the working substance is, in the end, brought back to its initial condition.

Efficiency of a Heat Engine

Def. "The efficiency of a heat engine is the ratio of the amount of heat which an engine converts into work to the total amount received from the source."

Thus, if

$$W = \text{area } ABCD,$$

$$\frac{W}{J} = \text{heat equivalent of the work performed.}$$

By the First Law of Thermodynamics

$$\frac{W}{J} = Q_1 - Q_2.$$

If E = efficiency of the engine,

$$E = \frac{\frac{W}{J}}{Q_1}$$

$$= \frac{Q_1 - Q_2}{Q_1}.$$

Example

One pound of coal, when burnt completely, gives about 14,000 British Thermal units (lb. F.° units). An economical engine is found to need about 1·3 lbs. of coal to be burnt per hour for each Horse Power developed. Taking the mechanical equivalent of heat as 778 ft. lbs. per British Thermal unit, calculate the efficiency of the engine.

Heat produced by 1·3 lbs. of coal per hour

$$= 14{,}000 \times 1{\cdot}3$$

$$= 18{,}200 \text{ units.}$$

$$\therefore \text{ Heat produced per min.} = \frac{18{,}200}{60}$$

$$= \frac{910}{3} \text{ units.}$$

$$\text{Work developed per min.} = 33{,}000 \text{ ft. lbs.}$$

Heat equivalent of work developed per min.

$$= \frac{33{,}000}{778} \text{ units.}$$

$$\text{Efficiency} = \frac{\frac{W}{J}}{Q_1}$$

$$= \frac{33{,}000}{778} \div \frac{910}{3}$$

$$= \frac{33{,}000 \times 3}{778 \times 910}$$

$$= {\cdot}14.$$

$$\text{Efficiency} = {\cdot}14 \text{ or } 14\,\%.$$

Carnot's Theorem

Def. "All reversible heat engines possess the same efficiency when absorbing and rejecting heat at the same two temperatures."

The truth of this theorem may be proved by showing that, if it were false, the Second Law of Thermodynamics would be violated.

Let us suppose that we are provided with two heat engines, A and B, both of which, when working *directly*, absorb heat from a source maintained at a temperature T_1 and reject heat into a condenser maintained at a temperature T_2.

If the efficiencies of A and B are not equal, *let us suppose that A has a greater efficiency than B.* Let us also suppose that in B the length of stroke is so adjusted that the work performed in a complete cycle is equal to that performed by A under similar circumstances.

By means of a suitable mechanism A may be coupled so that, when it works *directly*, it drives B *reversely*. Then during each complete cycle it will absorb a quantity Q_1 of heat at the temperature T_1 and reject a quantity Q_2 at a temperature T_2. On the other hand, since B traverses the cycle in a reverse sense, it will absorb a quantity Q_2' of heat at a temperature T_2 and reject a quantity Q_1' of heat at a temperature T_1.

Since equal amounts of work are performed in both cases, we have, in accordance with the First Law of Thermodynamics,

$$Q_1 - Q_2 = Q_1' - Q_2' \quad \ldots\ldots\ldots\ldots(1).$$

But, if the efficiency of A is greater than that of B, we must have

$$\frac{Q_1 - Q_2}{Q_1} > \frac{Q_1' - Q_2'}{Q_1'} \quad \ldots\ldots\ldots\ldots(2).$$

Dividing (2) by (1),

$$\frac{1}{Q_1} > \frac{1}{Q_1'},$$

$$\therefore\ Q_1' > Q_1 \quad \ldots\ldots\ldots\ldots(3).$$

Also from (3) and (1),

$$Q_2' > Q_2.$$

This means that the quantity Q_1' of heat which B discharges into the source is greater than the quantity Q_1 which it absorbs from the source, whilst the quantity Q_2' of heat which B absorbs from the condenser is greater than the quantity Q_2 of heat which it discharges into the condenser.

Hence, during the performance of each complete cycle, a quantity of heat equal to

$$Q_1' - Q_1 = Q_2' - Q_2$$

will be transferred from the condenser at T_2 to the source at a higher temperature T_1.

Since no external agency is supposed to aid the two engines, heat therefore passes from a body at a low to one at a higher temperature without the performance of work by external agency.

This is a violation of the Second Law of Thermodynamics.

$$\therefore\ Q_2' = Q_2,$$

$$Q_1' = Q_1,$$

$$\therefore\ \frac{Q_1' - Q_2'}{Q_1'} = \frac{Q_1 - Q_2}{Q_1},$$

i.e. the efficiencies of the two engines are equal.

Lord Kelvin's Absolute Scale of Temperature

Let AB, CD be two isothermals of a substance at any two temperatures. We will suppose that the temperature corresponding to AB is that of melting ice and CD that of water boiling under standard atmospheric pressure.

Take any point H on CD, and let HG be the adiabatic passing through this point, and let it cut the isothermal AB in G. Let the substance expand isothermally from H to E, and let GF be the adiabatic passing through the point E, and let it cut the isothermal AB in F.

Then the work done by a reversible heat engine, whilst describing the cycle $HEFG$ between the temperatures of boiling water and melting ice, will be equal to the area $HEFG$.

Now it is not necessary for us to go in one step from the isothermal CD to the isothermal AB. Let us divide the area $HEFG$ into any number of *equal* parts by means of isothermal lines such as KL, MN, PQ. We have thus divided the area $HEFG$ into four *equal* parts, but the most convenient number would be 100.

Then
$$\begin{aligned} \text{area } HELK &= \text{area } KLNM \\ &= \text{area } MNQP \\ &= \text{area } PQFG. \end{aligned}$$

Now let us define the temperature of any isothermal as *proportional* to the area enclosed by it and the two adiabatics HG, EF, and the isothermal AB.

Thus, since

$$\text{area } PQFG = \tfrac{1}{4} HEFG,$$

we may define the temperature corresponding to PQ as $25° + t°$, where $t°$ is the temperature corresponding to the isothermal AB. The temperature corresponding to MN will be $50° + t°$ and that corresponding to KL will be $75° + t°$.

To prove that temperatures measured on Lord Kelvin's Scale are independent of the nature of the substance of which the isothermals and adiabatics have been used

Let area $HEFG = A$,

t° = temperature measured on Lord Kelvin's Scale corresponding to any isothermal.

Then the area enclosed by the isothermals for t° and $(t-1)^\circ$ and the adiabatics HG and EF will be equal to $\frac{A}{100}$.

Now this area will be equal to the difference between the heat Q_1 absorbed at t° and the heat Q_2' rejected at $(t-1)^\circ$ by a reversible engine working between these temperatures.

$$\therefore\ Q_1 - Q_2' = \frac{A}{100}.$$

Similarly the area enclosed by two isothermals, corresponding to the temperatures t_1 and t_2, and the two adiabatics HG and EF, will be equal to $(t_1 - t_2)\frac{A}{100}$. Also, if Q_2 is the heat rejected at t_2 by a reversible engine working between t_1 and t_2, we have

$$Q_1 - Q_2 = (t_1 - t_2)\frac{A}{100} \quad \text{..........................(1).}$$

As a particular instance, let us suppose that the adiabatics HG and EF are prolonged until they cut the isothermal corresponding to the condition of a substance when entirely deprived of heat. If a reversible engine be supposed to work between the temperature t_1 and this latter temperature, no heat will be rejected from the engine at the lower temperature, since it is entirely deprived of heat; all the heat will have been converted into work during the adiabatic expansion.

Let us define the temperature of a substance, when entirely deprived of heat, as "the absolute zero of temperature." Then, in the above equation, if we measure temperatures from this zero, we shall have

$$Q_2 = 0,$$

$$t_2 = 0.$$

Substituting in (1),

$$Q_1 - 0 = (t_1 - 0)\frac{A}{100}.$$

$$\therefore\ Q_1 = t_1 \times \frac{A}{100} \quad \text{..................................(2).}$$

In obtaining (2) we have substituted particular values for Q_2 and t_2 in (1). But (1) is *generally* true for a heat engine absorbing a quantity Q_1 of heat at t_1 and rejecting a quantity Q_2 at t_2, where t_1 and t_2 are any temperatures measured on Lord Kelvin's Scale.

Dividing (1) by (2) we get,

$$\frac{Q_1 - Q_2}{Q_1} = \frac{t_1 - t_2}{t_1}.$$

But $\frac{Q_1 - Q_2}{Q_1}$ is the efficiency of a heat engine working between the isothermals corresponding to t_1 and t_2. By Carnot's Theorem this is independent of the nature of the substance used to transform heat into work.

$\therefore \frac{t_1 - t_2}{t_1}$ is independent of the nature of the substance used.

But

$$\frac{t_1 - t_2}{t_1} = 1 - \frac{t_2}{t_1}.$$

Hence, since 1 is a number and is therefore incapable of variations, the ratio $\frac{t_2}{t_1}$ of any two temperatures must be independent of the nature of the substance of which the isothermals and adiabatics have been used. That is, any substance, of which the isothermals and adiabatics can be determined, will serve equally well for measuring temperature, and the result obtained will be exactly the same whatever the substance used.

Further, since

$$\frac{Q_1 - Q_2}{Q_1} = \frac{t_1 - t_2}{t_1},$$

$$1 - \frac{Q_2}{Q_1} = 1 - \frac{t_2}{t_1}.$$

$$\therefore \frac{t_2}{t_1} = \frac{Q_2}{Q_1},$$

i.e. the ratio of any two temperatures is equal to the ratio of the heat absorbed to the heat rejected by an ideal heat engine working between these two temperatures.

Comparison of Lord Kelvin's Absolute Scale with the Air Thermometer Scale

It can be shown that Lord Kelvin's Absolute Scale nearly coincides with the air thermometer scale. The working out of this is a long and somewhat complicated affair.

Advantage of Lord Kelvin's Absolute Scale of Temperature

We have seen that the temperatures measured on Lord Kelvin's Scale are *independent of the nature of the substance* of which the isothermals and adiabatics have been used. This is a most important point.

In measuring temperatures by the *expansion* of some substance the magnitude of a degree depends more or less upon the nature of the substance. This is clear if we recall the expansion of water, for example. Even with a gas thermometer the magnitude of a degree will vary according as Carbon Dioxide or Hydrogen, for instance, is used.

In the case of Lord Kelvin's Absolute Scale, since

$$\frac{t_2}{t_1} = \frac{Q_2}{Q_1} = \frac{\text{work}}{\text{work}},$$

the ratio of any two temperatures may be obtained in absolute units and will be independent of the particular substance used.

Lord Kelvin's thermodynamic scale of temperature is therefore *absolute* in the true sense of the term, i.e. it is *based upon the absolute units.*

Entropy

In passing along an adiabatic, such as *abcde*, successive changes of temperature are experienced by a substance. At e the temperature of the substance may be, for instance, that of water boiling under standard conditions, whilst at a the temperature may be that of melting ice. All intermediate temperatures will be successively attained in passing from a to e.

Moreover, in passing from one isothermal to another, the same alteration in temperature will be experienced, no matter what adiabatic is traversed. Thus, since d and d_1 are on the same isothermal DD_1, these points will correspond to equal temperatures. Similarly e and e_1 will correspond to equal temperatures. Therefore, in passing from d to e, the rise in temperature will be equal to that on passing from d_1 to e_1.

Now let us consider *the thermal changes that take place during the passage along an isothermal from one adiabatic to another.* Though the temperature remains constant, a certain quantity of heat enters the body if external work is performed by it (or if its internal energy is increased) or is rejected by the body if work is performed on it by external agency (or if its internal energy is diminished).

Now during the passage along different isothermals *equal quantities of heat will not be absorbed or rejected between the same adiabatics.* Thus, if Q_1 units of heat are absorbed passing from e to e_1 at the constant temperature t_1, then Q_2 units will be given up during the passages from d_1 to d at the constant temperature t_2, the relations between Q_1 and Q_2 being expressed by the equations

$$Q_1 - Q_2 = \text{area } ee_1d_1d,$$

$$\frac{Q_1 - Q_2}{Q_1} = \frac{t_1 - t_2}{t_1},$$

$$\frac{Q_2}{Q_1} = \frac{t_2}{t_1},$$

$$\frac{Q_2}{t_2} = \frac{Q_1}{t_1}.$$

Further, the above operations are reversible, i.e. if Q_2 units of heat are given up during a compression from d_1 to d at a temperature t_2, Q_2 units will be absorbed during an expansion from d to d_1.

In the same way, if Q_3 units of heat are absorbed in passing from c to c_1 at the constant temperature t_3,

$$\frac{Q_3}{t_3}=\frac{Q_2}{t_2}=\frac{Q_1}{t_1},$$

where t_3, t_2, t_1 are absolute temperatures.

Hence, in passing along *any* isothermal from one adiabatic to another, the ratio

$$\frac{\text{heat absorbed (or rejected)}}{\text{absolute temperature corresponding to isothermal traversed}}$$

will be *constant*, whatever isothermal path is chosen.

This ratio may be used to distinguish different adiabatics, just as different isothermals are distinguished by their temperature.

Let us take any adiabatic $edcba$ as a standard and draw the adiabatic $e_1d_1c_1b_1a_1$, so that

$$\frac{Q_1}{t_1}=\frac{Q_2}{t_2}=\frac{Q_3}{t_3}=1.$$

We might then draw another adiabatic $e_2d_2c_2b_2a_2$, so that the ratio

$$\frac{\text{heat absorbed during the passage to it from } e_1d_1c_1b_1a_1}{\text{absolute temperature corresponding to isothermal traversed}}$$

was once more equal to 1.

Proceeding in this way we might divide the whole of the diagram up by consecutive adiabatics, distinguished by the characteristic that, in passing *isothermally* from one to another,

$$\frac{\text{heat absorbed (or rejected)}}{\text{absolute temperature corresponding to isothermal traversed}}=1.$$

This characteristic property distinguishing one adiabatic from another is termed "difference of entropy."

All points on an adiabatic will be characterised by the same entropy. It is on this account that adiabatics are sometimes called "isentropics," i.e. lines of equal entropy.

When heat enters a substance its entropy increases. The increase in entropy is measured by $\frac{Q}{t}$,

where Q = heat absorbed,
t = absolute temperature during the absorption.

1st Def. "Entropy is the thermal property of a substance which remains constant as long as heat is not communicated to, or abstracted from, it by external bodies."

2nd Def. "If a substance at a temperature t receives Q units of heat, it is said to receive $\frac{Q}{t}$ entropy."

INTERNAL WORK

Mayer in his work on the Mechanical Equivalent of Heat assumed that *a gas in free expansion does no work against internal forces.*

Experiments to test the truth of this assumption were made by

1. Joule.
2. Joule and Lord Kelvin.

The idea underlying their experiments was as follows:—

When a gas expands *doing external work* its temperature falls, unless heat is communicated to it. The problem was to ascertain if any temperature change takes place when a gas expands *without doing external work.* Such a change in temperature might be due to one of two things:—

1. To the work done *on* the molecules.

There might be an *attraction* between the molecules and, when you separated them, there would be *an increase in the potential energy.* But since the sum of the potential and kinetic energies is constant, if the potential energy increases, the kinetic decreases and you get a *fall in temperature.* Compare the case of an elastic band on being pulled out.

2. To the work done *by* the molecules.

There might be a *repulsion* between the molecules and, when you separated them, there would be *a decrease in the potential energy.* If the potential energy decreases, the kinetic energy increases and you get a *rise in temperature.* Compare the case of a compressed spring on being let go.

Joule's Experiments

To see if any such change in temperature took place, Joule made two experiments:—

1. Two metal vessels, connected by a stop-cock, were enclosed in a calorimeter containing water. One was exhausted and the other was filled with gas under a pressure of 22 atmos. On opening the stop-cock there was *no resultant change in temperature.*

2. Two metal vessels were enclosed in separate calorimeters. The loss of heat in one calorimeter was very nearly equal to the gain of heat in the other.

In (2) there is a fall in temperature in one vessel due to the work done *by* the remaining gas in pushing out that which has passed into the second vessel and a rise in

temperature in the other vessel due to the work done *on* the gas already in the second vessel, as successive portions entered and compressed it.

Joule concluded from these experiments that there was *no fall or rise in temperature due to the internal work done by gases in expanding,* i.e. that no internal work is done when a gas expands or, in other words, that the molecules of a gas are so far removed from each other that the effects of their mutual attractions or repulsions may be neglected.

Joule's failure to show that some internal work *is* done by gases in free expansion was probably due to the nature of his experiment, which was not a very delicate one, since the thermal capacity of the calorimeter and water was many times greater than that of the gas. He was, moreover, dealing with large quantities of water, which made a slight change in temperature very difficult to observe. What Joule really proved was that *no heating or cooling effect, of any considerable magnitude,* is associated with the free expansion of gases, when no external work is performed.

The weak point in Joule's experiment was the use of water to indicate, by its change in temperature, whether heat disappeared or was generated in the expanding gas. It can readily be shown that, though Joule used a thermometer which was capable of indicating a difference in temperature of $\frac{1}{200}$ F.°, no heating or cooling effect, *unless of a considerable magnitude,* could possibly have been detected by the method he employed.

Specific heat of air at constant volume = ·17.

Volume of 1 gm. of air at 0° C. and 760 mm. = 773·4 c.c.

To raise 1 gm. of air through 1 C.° requires ·17 cal.

But ·17 cal. raises 1 gm. of water through ·17 C.°

Let us suppose there were 1000 gms. of water.

·17 cal. raises 1000 gms. of water through $\frac{\cdot 17}{1000} = \cdot 00017$ C.°

This amount was altogether inappreciable in Joule's experiment.

It should be noted, however, that if the pressure was 22 atmos., the mass of gas employed was, probably, much more than 1 gm. But even then the rise in temperature would be scarcely capable of detection.

Joule and Lord Kelvin's Porous Plug Experiment

Certain considerations lead Joule and Lord Kelvin to conclude that, though there should be no heating or cooling of a perfect gas on free expansion, gases which do not obey Boyle's Law should exhibit a small thermal change under the same conditions. They therefore determined to investigate the phenomena, using a method in which the temperature of the gas could be *directly* measured and not that of the water surrounding it.

Ideal arrangement illustrating the character of the process employed

Let us suppose we are provided with a long cylinder, *CD*, fitted with two air-tight and frictionless pistons, *A* and *B*, and possessing a diaphragm *E*, pierced by a small aperture.

Let us suppose that *the piston B is initially pressed close up to the diaphragm E*, whilst 1 gm. of *compressed gas*, at a pressure p_1, is introduced into the part of the cylinder between *A* and *E*. The walls of the cylinder are assumed to be *perfect non-conductors of heat.* Thus, if T° is the initial temperature of the gas, any change from the temperature *can only be produced by the performance of work on or by the gas*, and not by the direct transference of heat.

Let the motion of the piston *B* be opposed by a uniform force F_2.

Let a = area of either piston.

Then the piston *B* will move outward uniformly when the pressure of the gas between *E* and *B* has attained a value p_2 such that

$$p_2 a = F_2.$$

Let the force tending from the first to force the piston *A* *inwards* be F_1. Then, as the gas passes through the orifice in *E*, so as to press the piston *B* forwards, the piston *A* will move inwards towards *E* at such a rate that the pressure p_1 of the air between *A* and *E* remains constant.

Then $p_1 a = F_1$.

Let v_1 = initial volume of gas contained in *AE*,

x_1 = initial distance between *A* and *E*.

Then $ax_1 = v_1$.

When the piston *A* has moved up to the diaphragm *E*, the whole of the air will have been forced from *AE* into *EB*.

Let v_2 = volume occupied by air in *EB*,

x_2 = distance through which piston *B* has moved.

Then $ax_2 = v_2$.

Since no heat can enter or leave the cylinder, any change in the energy of the contained gas must be due to the performance of work on or by the gas.

Let E_1 = internal energy possessed by gas when in *AE*,

E_2 = internal energy possessed by gas when in *EB*.

Work performed by external agency *on* the gas

$$\begin{aligned} &= \text{force} \times \text{distance} \\ &= F_1 \times x_1 \\ &= p_1 a x_1 \\ &= p_1 v_1. \end{aligned}$$

Work performed *by* the gas

$$
\begin{aligned}
&= \text{force resisting motion} \times \text{distance}\\
&= F_2 \times x_2\\
&= p_2 a x_2\\
&= p_2 v_2.
\end{aligned}
$$

The difference between the final and initial energies of the gas must be equal to the difference between the work performed *on* the gas and the work performed *by* the gas.

$$\therefore\ p_1 v_1 - p_2 v_2 = E_2 - E_1.$$

Now the energy possessed by the molecules of the gas may be partly kinetic and partly potential. The kinetic energy we have learnt to associate with heat. The potential energy will depend upon the *relative position of the molecules*, supposing that attractive or repulsive forces are exerted between them.

We may consider the three following cases:—

1. Let $$p_1 v_1 = p_2 v_2,$$

i.e. the gas obeys Boyle's Law.

In this case $$E_1 = E_2.$$

If there is any *attractive force* between neighbouring molecules, this force must have been overcome during the expansion of the gas, and consequently the potential energy of the molecules must be greater in the final than in the initial condition. But the *total* energy has the same value in both cases. Therefore the kinetic energy will be less in the final than in the initial condition. The result will be that the gas will be *cooled* during the expansion.

If there is a *repulsive force* between neighbouring molecules, the potential energy of the molecules will be diminished during expansion and consequently their kinetic energy will increase. The result will be that the gas will be *heated* during the expansion.

2. Let $$p_1 v_1 < p_2 v_2.$$

In this case the product *pv decreases* as the pressure is *increased*. This is usually the case during the initial stages of the compression of a gas, though hydrogen is an exception. (See the work of Regnault and Amagat.)

Since
$$
\begin{aligned}
p_1 v_1 - p_2 v_2 &= E_2 - E_1,\\
E_2 - E_1 &= \text{some negative value}\\
&= -e.\\
\therefore\ E_2 &= E_1 - e,
\end{aligned}
$$

i.e. the energy possessed by the gas is *less* in the final than in the initial condition.

Therefore, *if no forces are exerted between neighbouring molecules*, a slight *cooling* effect will be produced.

If molecular *attractions* are exerted, a still greater cooling will result.

If molecular *repulsions* are exerted, the cooling due to the divergence from Boyle's Law may be partially or entirely compensated for, or a heating effect may be produced.

3. Let $$p_1 v_1 > p_2 v_2.$$

In this case the product pv *increases* as the pressure is *increased.* Regnault and Amagat found this to be the case with hydrogen, and Amagat showed that it is also the case with most gases when subjected to very high pressures.

Since
$$p_1 v_1 - p_2 v_2 = E_2 - E_1,$$
$$E_2 - E_1 = \text{some positive value}$$
$$= e.$$
$$\therefore\ E_2 = E_1 + e.$$

A *heating* effect will be produced, *if no molecular forces are exerted.*

If molecular *repulsions* exist, this heating effect will be increased.

If molecular *attractions* exist, a smaller heating effect, or even a cooling effect, may be produced.

Modifications of the ideal arrangement

1. The piston B may be dispensed with. The pressure p_2 will then be equal to the atmospheric pressure.

2. Care must be taken that the jet of air issuing from the orifice does not produce any sound.

3. Instead of forcing the piston A along the cylinder, the end, C, of the cylinder may be connected to a pump, provided the action of the pump is such that the pressure of the gas is maintained constant on the left-hand side. It is essential that the gas between the orifice and the pump should be maintained at a constant temperature and pressure.

The Porous Plug Experiment

To avoid the production of eddy currents in the gas, a plug of cotton wool, A, was substituted for the perforated diaphragm. By this means a large number of very small orifices were obtained instead of a single one. The cotton wool was held in position by two metal discs, about 3 ins. apart, pierced with many holes. To avoid loss or gain of heat in the neighbourhood of the plug, it was enclosed in a hollow boxwood cylinder, BC, which was surrounded by cotton wool packed in a metal vessel, D. The gas was conveyed to the plug by a metal tube, E, which formed the end of a long spiral tube immersed in a water bath. A delicate thermometer was placed so that its bulb was immediately above the plug. The gas was compressed by a pump, P, and then caused to traverse two long copper spirals immersed in water baths, the temperatures of which were maintained constant throughout the experiment. During the compression of the gas in P heat was produced and the object of the baths was to keep the temperature of the gas as constant as possible.

Results of Joule and Lord Kelvin's Experiment

1. Air, oxygen, nitrogen and carbon dioxide were all *cooled* by expansion.

2. The cooling was *most noticeable* in the case of carbon dioxide, the least perfect of the gases.

3. With hydrogen a small *heating* effect was observed.

4. The thermal effect produced was *proportional to the difference between the pressures* on the two sides of the plug.

5. At high temperatures the cooling effect was less than at low temperatures. Its magnitude *varied inversely as the square of the absolute temperature of the gas.*

6. The actual values obtained in some experiments were as follows:—

(1) Air.

Mean temperature during experiment	Fall in temperature on free expansion for a difference of pressure of 1 atmo.
7° C.	·263 C.°
26° C.	·229 C.°
50° C.	·209 C.°
93° C.	·152 C.°

(2) Carbon dioxide.

Mean temperature during experiment	Fall in temperature on free expansion for a difference of pressure of 1 atmo.
8° C.	1·233 C.°
36° C.	1·022 C.°
54° C.	·885 C.°
96° C.	·645 C.°

(3) Hydrogen.

A rise in temperature of ·039 C.° on free expansion was observed for a difference of pressure of 1 atmosphere.

Explanation of the results obtained

(1) Air.

Amagat showed that, in the case of air, the product *pv decreases for an increase of pressure* from 1 to 31 atmospheres, i.e.

$$p_2v_2 > p_1v_1,$$

work done *by* the gas > work done *on* the gas. This would produce a certain amount of *cooling*.

Now it is possible to calculate what the cooling should be for a given pressure. If we do so, we find that, in one case, where it should be ·1 C.°, the cooling actually observed was ·9 C.°

The conclusion is that some of the energy was also taken up in the separation of the molecules, i.e. *there was an increase in the internal energy in expansion*, i.e. *there was a gain in potential and a corresponding loss in kinetic energy.*

(2) Carbon Dioxide.

In the case of carbon dioxide it was found that the cooling was chiefly due to a change in the internal energy.

(3) Hydrogen.

In the case of hydrogen the product *pv increases with pressure,* i.e.

$$p_1v_1 > p_2v_2,$$

work done *on* the gas > work done *by* the gas. This would produce a certain amount of *heating.*

The actual effect observed was a slight heating and of such an order that it was probably due to Boyle's Law being untrue. Hence it was concluded that the change in internal energy is very small *at ordinary temperatures. At low temperatures* the behaviour of hydrogen appears to be different, i.e. a cooling effect is observed. This makes the liquefaction of hydrogen by the "self-intensive method" possible.

Summary of the conclusions arrived at by Joule and Lord Kelvin

1. At ordinary temperatures molecules of air, nitrogen, oxygen and carbon dioxide exert a small but appreciable *attractive force* upon one another. On free expansion there is therefore a gain in potential energy and a corresponding loss in kinetic energy, which causes a fall in temperature.

2. *At ordinary temperatures* molecules of hydrogen appear to exert a small *repulsive force* upon one another. On free expansion there is therefore a loss in potential energy and a corresponding gain in kinetic energy, which causes a rise in temperature.

At *low temperatures* molecules of hydrogen appear to exert an *attractive force* upon one another. On free expansion a fall in temperature takes places.

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